

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 10-175365

(43)Date of publication of application : 30.06.1998

(51)Int.Cl.

B41M 5/00
C09J129/04

(21)Application number : 08-339539

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(22)Date of filing : 19.12.1996

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(54) INK JET RECORDING METHOD

(57)Abstract:

PROBLEM TO BE SOLVED: To provide the high glossiness and the quick drying properties and good physical properties of a film after printing to be compatible each other when the ink jet recording is carried out by using an aqueous ink on an ink jet recording paper with an ink absorbent layer constituted of a space structure on a low-water-absorbent substrate.

SOLUTION: Recording is carried out by using water-soluble inks of colors of at least yellow, magenta and cyanogen on a recording paper with an ink absorption layer on a non-water-absorbent substrate in a recording method. In that case, a recording paper is provided with space layers containing a hydrophilic binder and secondary fine particles of average particle diameter of 30-200nm, and the space volume of the space layers is three times or more the volume of a high boiling point organic solvent contained in the ink when the ink discharge amount is maximum.

LEGAL STATUS

[Date of request for examination] 14.09.2001

[Date of sending the examiner's decision of rejection] 11.11.2003

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection] 2003-24062

[Date of requesting appeal against examiner's decision of rejection] 11.12.2003

[Date of extinction of right]

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CLAIMS

[Claim(s)]

[Claim 1] In the ink jet record approach which records on a non-absorptivity base material by using yellow, a Magenta, and the water-soluble ink of cyanogen for the record form which has an ink absorptivity layer at least These record forms are a hydrophilic binder and an ink jet record form which has an opening layer containing the secondary particle which has a 30-200nm mean diameter. The ink jet record approach characterized by the void volume of this opening layer being 3 or more times of the capacity of the high-boiling point organic solvent which ink in case ink discharge quantity is max contains.

[Claim 2] The ink jet record approach according to claim 1 characterized by said secondary particle being a silica.

[Claim 3] The ink jet record approach according to claim 1 or 2 characterized by the ratios to the hydrophilic binder of said secondary particle being 4-10 in a weight ratio.

[Claim 4] The ink jet record approach according to claim 1, 2, or 3 characterized by said hydrophilic binder being polyvinyl alcohol.

[Claim 5] The ink jet record approach of claim 1-4 characterized by said opening layer containing a hardening agent given in any 1 term.

[Claim 6] The ink jet record approach of claim 1-5 given in any 1 term that the amount of the high-boiling point organic solvent which said water-soluble ink contains is characterized by being below 35 capacity % to the capacity of ink.

[Claim 7] The ink jet record approach of claim 1-6 characterized by being the paper base material with which said non-absorptivity base material covered both sides with polyolefine given in any 1 term.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the ink jet record approach of could record the color picture which has a high-class feeling by high definition without high glossiness and nonuniformity especially about the color ink jet record approach which records using water color ink, and having improved the handling nature immediately after record.

[0002]

[Description of the Prior Art] although ink jet record makes the minute drop of ink fly by various working principles, and is made to adhere to record sheets, such as paper, and an image, an alphabetic character, etc. are recorded, a high speed, the low noise, and multiple-color-izing are comparatively easy — etc. — it has the advantage. About the blinding of a nozzle and the maintenance which had become a problem from the former by this method, from both sides of ink and equipment, amelioration progresses and it has spread through various fields, such as various printers, facsimile, and a computer terminal, quickly in current.

[0003] The detail is indicated by the trend (the volume for Koichi Nakamura, March 31, Heisei 7, the Japan science-information incorporated company issue) of for example, an ink jet record technique.

[0004] As a record form used by this ink jet recording method, also when a printing dot laps [that a color tone is brightly skillful and absorption of ink] early, the diffusion to the longitudinal direction of ink flowing out or not spreading and a printing dot is not large [the concentration of a printing dot is high, and] beyond the need, and generally it is required that the circumference should be smooth and should not fade etc.

[0005] By the way, many attempts which are going to bring the image quality acquired by color ink jet record close to a photograph are performed in recent years.

[0006] This is roughly divided into the property related to an ink absorptivity layer, the property about amelioration of the image quality resulting from the dot formed in a record form, and the property related to a base material.

[0007] Or it raises the smooth nature on the front face of ink which raises the transparency of an ink absorptivity layer and improves printing concentration as an attempt which improves an ink absorptivity layer and raises glossiness, the maximum ink absorption capacity is secured enough, it is making it ink not overflow in a maximum-density region, and the extensive amelioration technique has been proposed from the former.

[0008] on the other hand, the greatest point of the improvement in image quality resulting from a dot be that one one piece dot prevent from identify visually, therefore it be the point to form a liquid ink drop into a small drop, to use low-concentration ink together as color concentration, in order that discernment of the dot in the highlights section may carry out as [be / difficult] especially, etc., and in order to improve this point, various amelioration techniques have be propose from the former.

[0009] Moreover, in the regular paper and paper of fine quality with which ink tends [comparatively] to permeate as a record form or the usual art paper, or the comparatively big cast coated paper of absorptivity, since ink permeates into a base material, a wrinkling occurs after record only in the printing section, and print quality is reduced greatly. Moreover, since ink permeates into paper fiber or permeates into an opaque high white-pigments content coat layer, there is a fault from which a clear image is hard to be obtained that it is hard to come out of maximum density.

[0010] Furthermore, since the white pigments of paper fiber or comparatively big size exist [the roundness of a dot], it is also the cause of degradation of the image quality at the time of turbulence and this carrying out ink jet record.

[0011] In order to acquire image quality with a high-class feeling like a photograph as an ink jet record form from the above point, For example, the base material for photographs with which water color ink cannot permeate easily, the record form (it Bulletein(s) (Vol.21, NO. 1978 [6 or], 2502 pages) for example, IBM Technical Disclosure [] —) which applied the ink absorptivity layer on the paper base material for the photographs which covered especially both sides with polyolefine U.S. Pat. No. 3,889,270, JP,7-179032,A, 7-179025, And it is indicated by 7-32723 and the 8-174992 official report, the record form (for example, indicated by JP,61-

135783,A) which applied the ink absorptivity layer on white plastic film is used increasingly preferably.

[0012] By the way, in order to attain the image quality of the above-mentioned photograph average, it is, Although it is that especially the thing established for an ink absorptivity layer with comparatively high transparency on the base material of low ink absorptivity is desirable, when the front face of an ink absorptivity layer mat-izes, and carries out a gloss fall or the ink absorption layer itself has the quite big microstructure, the opacity of an ink absorptivity layer goes up in addition to the fall of gloss, and it is hard to attain about the same image quality as a photograph in many cases.

[0013] Although many things are known from the former as an ink absorptivity layer prepared on a base material, it is roughly classified into two types.

[0014] One of them is the ink absorptivity layer of a swelling mold, and it is an ink absorptivity layer which makes a hydrophilic binder a subject. As for this, a liquid ink drop evaporates the moisture of a hydrophilic binder which holds temporarily mainly according to a swelling operation, and ink contains gradually after printing, and a high-boiling point organic solvent.

[0015] The advantage of the swelling mold record form which prepared this ink absorptivity layer on the base material is in the point that very high glossiness and high maximum density are obtained, after an ink solvent (water and high-boiling point organic solvent) evaporates completely. On the other hand, this swelling mold record form is late compared with the opening mold record form which ink rate of absorption mentions later, there is a problem to which beading etc. is cause in a high ink field and image quality tends to fall, and there is a problem accompanying be put on the damp or wet condition which the hydrophilic binder swelled for a while since evaporation of an ink solvent, especially a high-boiling point organic solvent is still very slower, after print for a long period of time. Specifically, it is in the situation that a printing front face cannot be strongly ground for several days by the case for several after [printing] hours, or paper etc. cannot be piled up.

[0016] As an ink absorptivity layer of a mold other than the above-mentioned swelling mold, there is an opening mold record form with which an ink absorptivity layer has opening structure. By holding ink temporarily to this opening in the case of ink jet record, this record form absorbs ink and there is [in / in ink rate of absorption / a high ink field] little degradation of image quality early compared with a swelling mold.

[0017] Moreover, though the organic solvent remained in opening structure when this kind of ink absorptivity layer had void volume of enough to the amount of ink, at least, a front face will be seemingly got dry immediately after printing, a front face is touched or it becomes once possible to pile up prints etc.

[0018] Especially the silica particle that a particle with a particle size small moreover (especially 200nm or less is desirable) is preferably used from the point that a layer with comparatively high transparency is formed, as this kind of an ink absorptivity layer with a low refractive index (about 1.6 or less refractive index is especially desirable), and fulfills these conditions especially is desirable.

[0019] As a conventional technique which uses such a particle silica for an ink JIETO record form, JP,3-56552,B is made to condense the secondary particle silica obtained by the gaseous-phase method primary particle size is 10-30nm, and the record form which has the ink absorption layer which the surface area by the BET adsorption method makes form the particle which is 80-200m²/g, and contains is indicated.

[0020] Moreover, for said JP,8-174992,A, a mean diameter uses a non-subtlety particle and a hydrophilic binder 10nm or less on a polyolefine covering paper base material, and the ink jet record form which obtains high glossiness is indicated.

[0021] However, the inclination for the physical reinforcement of surface glossiness and the front face after printing to conflict in the case of the ink absorptivity layer which has opening structure is large.

[0022] That is, although it will be hard to produce the problem referred to as that ink imprints it even if the reinforcement of the front face after printing is good, and it touches a front face or it piles up paper etc. if the magnitude and the micro opening structure of a particle which are contained there exceed 200 micrometers when an opening layer is seen in micro, the inclination for glossiness to fall extremely is large.

[0023] Moreover, if the magnitude and the micro opening structure of a particle are set to 200nm or less, although gloss will improve gradually, the trace becomes easy to remain, when the softness of the front face after printing increases, the sample was piled up, an ink imprint begins to take place partially or paper is written to an ink absorption stratification plane side with a pencil etc. from on the in piles. This problem will become still larger if especially opening structure is set to 100nm or less.

[0024] If the softness of the front face immediately after this printing is compared with the surface state of the aforementioned swelling mold ink absorptivity layer, it is in the level expected amelioration of a far good thing.

[0025] Although the time amount to which the moisture itself remains in an opening layer although moisture and a high-boiling point organic solvent are one of causes of the problem related to the reinforcement of the coat after such printing cannot become the problem that such a problem is not much big, comparatively easily because of a short time, generally evaporation of a high-boiling point organic solvent tends to receive constraint in handling nature in the meantime, in order for a room temperature to take the time amount of several days.

[0026] When the print after printing is saved with a high-humidity state, since more many moisture is maintained

by the coat, this problem tends to change notably. Moreover, this problem tends to arise in the part by which the peak of the amount of ink was breathed out.

[0027] It is presumed that it is because the structure of a coat became is easier to be destroyed by the force applied from the outside when a touch area with the paper which the irregularity of the front face of an ink absorptivity layer becomes small one, and is piled up although the reason of why becoming easy to produce this problem when opening structure is set to 200nm or less is not certain becoming large, and opening structure made it detailed.

[0028] Although the record form which used this particle silica has comparatively high ink absorptivity and glossiness, the solution over the above mentioned technical problem is not given to said JP,8-174992,A and JP,3-56552,B.

[0029]

[Problem(s) to be Solved by the Invention] The technical problem which this invention is made in view of the above-mentioned actual condition, and this invention tends to solve is to offer the ink jet record approach of having reconciled high-glossiness, drying [with the early coat after printing], and a good physical property, in case water color ink is used for the ink jet record form which has the ink absorptivity layer which consists of opening structure on a low absorptivity base material and ink jet record is carried out.

[0030]

[Means for Solving the Problem] In the ink jet record approach which records at least the technical problem which above-mentioned this invention tends to solve in yellow, a Magenta, and the water-soluble ink of cyanogen on the record form which has an ink absorptivity layer on a non-absorptivity base material These record forms are a hydrophilic binder and an ink jet record form which has an opening layer containing the secondary particle which has a 30-200nm mean diameter. It is attained by the ink jet record approach characterized by the void volume of this opening layer being 3 or more times of the volume of the high-boiling point organic solvent which ink in case ink discharge quantity is max contains.

[0031] This invention is explained to a detail below.

[0032] As a non-absorptivity base material used for the record form of this invention, the paper base material which covered plastic film and both sides with polyolefine is used preferably.

[0033] As a plastic film base material, plastic film base materials, such as polyethylene, polypropylene, polystyrene, polyethylene terephthalate, polyethylenenaphthalate, triacetyl cellulose, a polyvinyl chloride, polyimide, a polycarbonate, and cellophane, etc. are desirable, for example.

[0034] These plastic film can use suitably a transparent thing, a translucent thing, and an opaque thing properly according to an application.

[0035] When considering as a white film, you may be the base material which prepared the layer which may use the base material which the plastic film base material was made to contain white pigments, such as a small amount of barium sulfate, titanium oxide, and a zinc oxide, and was obtained as it is, and has white pigments (titanium oxide, barium sulfate, etc.) in the side near the base material by the side of the rear face of a transparent film base material, or an ink absorptivity layer.

[0036] Moreover, the paper base material which covered both sides with the polyethylene usually conventionally used in color printing paper as a paper base material which covered both sides with polyolefine is desirable. In this case, it is desirable to make the titanium oxide of an anatase mold or a rutile mold contain three to 20% of the weight to polyethylene in the polyethylene resin layer by the side of an ink absorptivity layer from there not being even improvement in the opacity of a base material or a whiteness degree or a fall of the sharp nature of an image obtained.

[0037] In this invention, a white film base material or the paper base material which covered both sides with polyolefines, such as polyethylene, is desirable, and the paper base material which covered both sides with the polyolefine which has a high-class feeling especially by low cost is the most desirable than the viewpoint which obtains a high-definition color picture.

[0038] Hereafter, especially the paper base material that covered both sides with the polyethylene used preferably is explained.

[0039] The stencil paper used for a paper base material uses wood pulp as the main raw material, and, in addition to wood pulp, paper making is carried out using synthetic fibers, such as synthetic pulps, such as polypropylene, or nylon, and polyester, if needed. Although both LBKP, LBSP, NBKP, NBSP LDP and NDP LUKP and NUKP can be used as wood pulp, it is desirable to use more many [for a staple fiber] LBKP, NBSP(s), LBSP(s), and NDP (s) and LDP(s). However, it reaches LBSP or the ratio of LDP has 10 % of the weight or more and 70 desirable % of the weight or less.

[0040] The pulp of the above-mentioned pulp which chemical pulp with few impurities (sulfate pulp and sulfite pulp) was used preferably, and performed bleaching processing, and raised the whiteness degree is also useful.

[0041] Hara Kaminaka can add suitably flexible-ized agents, such as moisture hold-back agents, such as paper reinforcing agents, such as white pigments, such as sizing compounds, such as a higher fatty acid and an alkyl

ketene dimer, a calcium carbonate, talc, and titanium oxide, starch, polyacrylamide, and polyvinyl alcohol, a fluorescent brightener, and polyethylene glycols, a dispersant, and the 4th class ammonium, etc.

[0042] The freshness of the pulp used for paper making has desirable 200–500 cc by convention of CSF, and 30 thru/or 70% have the desirable sum of 24-mesh residue weight % and weight % for 42-mesh ** as which the fiber length after beating is specified to JIS-P -8207. In addition, as for weight % of the four-mesh residue, it is desirable that it is 20 or less % of the weight.

[0043] The basis weight of stencil paper has 60 thru/or desirable 250g, and 90 thru/or especially its 200g are desirable. The thickness of stencil paper has 50 thru/or desirable 250 micrometers.

[0044] After a paper-making phase or paper making, calender processing of the stencil paper can be carried out, and it can also give the Takahira slippage. A stencil paper consistency has 0.7 thru/or common 1.2 g/m² (JIS-P -8118). Furthermore, stencil paper stiffness has 20 thru/or desirable 200g on the conditions specified to JIS-P -8143.

[0045] A surface sizing compound may be applied to a stencil paper front face, and the sizing compound which can be added to said Hara Kaminaka as a surface sizing compound, and the same sizing compound can be used.

[0046] When pH of stencil paper is measured by the hot water extraction method specified by JIS-P-8113, mainly although the polyethylene with which that it is 5–9 cover a desirable stencil paper front face and a desirable rear face is the polyethylene (LDPE) of a low consistency, and/or polyethylene (HDPE) of high density, a part of other LLDPE(s), polypropylene, etc. can be used for it.

[0047] As for especially the polyethylene layer by the side of an ink absorbing layer, what added the titanium oxide of a rutile or an anatase mold in polyethylene as widely performed by the printing paper for photographs, and improved opacity and a whiteness degree is desirable. A titanium oxide content is 5 – 15 % of the weight preferably three to 20% of the weight in general to polyethylene.

[0048] polyethylene covering paper can also use the object in which a mat side which performs the so-called mold attachment processing and is acquired with the usual photographic printing paper, and the silky surface were formed, by this invention, in case melting push appearance also of also using as glossy paper is carried out and it coats polyethylene on a stencil paper front face.

[0049] After preparing an ink absorbing layer and a back layer, the amount of the polyethylene used of the front flesh side of stencil paper is damp and range whose 20–40-micrometer and back layer side the polyethylene layer by the side of an ink absorbing layer is 10–30 micrometers in general, although it is chosen so that the curl by highly-humid-izing may be optimized.

[0050] Furthermore, as for the above-mentioned polyethylene covering paper base material, it is desirable to have the following properties.

[0051] ** It is desirable that a lengthwise direction is [2 thru/or 30kg, and a longitudinal direction] 1 thru/or 20kg by the reinforcement specified by :JIS-P -8113 in hauling strength.

[0052] ** Tear reinforcement : 10 thru/or 300g, and a longitudinal direction have [a lengthwise direction] 20 thru/or desirable 400g by the convention approach by JIS-P -8116.

[0053] ** Clerks stiffness : 20–400g/100 are desirable.

[0054] ** Compressibility ≥ 103 kgf/cm² ** surface smoothness : 500 seconds or more, although the Beck smoothness specified to JIS-P-8119 has 1000 desirable seconds or more especially as a glossy surface, it may be less than [this] in the so-called mold attachment article.

[0055] ** surface roughness: — the wave filtration waviness curve drawn on with a cut-off value [of 0.8mm] conditions from the cross-section curve measured by the approach specified to JIS-B -0610 — a criteria tone — as 2.5mm — wave filtration max — the time of measuring a wave — 100 point of measurement of the arbitration — max — it is desirable that a wave is [a point 6 micrometers or more] less than five pieces and that the ten-point average of roughness height is less than 4 micrometers.

[0056] ** Surface glossiness : when it measures at the include angle of 60 degrees by the approach specified to JISZ-8741, it is 90% or more especially preferably 70% or more preferably 30% or more.

[0057] ** Surface whiteness degree : when it measures by the approach indicated by JIS-Z -8722 and displays according to JIS-Z -8729, [0058]

[External Character 1]

L*は85%以上、特に90%以上が好ましい。

また、(a*, b*)は(−2, 2)、(4, 2)、(4, −8)

および(−3, −8)で囲まれる範囲の色調が好ましい。

[0059] ** Opacity : when it measures by the approach specified to JIS-P -8138, it is especially most preferably [94% or more of] desirable 90% or more 50% or more.

[0060] 15–50 micrometers of thickness of the polyolefine layer which covers a paper base material are 20–40 micrometers preferably. In consideration of the balance of the curl after painting ink absorptivity being optimized, according to the view usually performed with the printing paper base material for photographs, the polyolefine

layer of the front flesh side of paper is optimized suitably, and is decided.

[0061] 100–300 micrometers of thickness of said base material are 130–250 micrometers preferably.

[0062] It is desirable to perform corona discharge treatment, undercoating processing, etc. to a base material in advance of spreading of an ink absorbing layer for the purpose, such as to enlarge bond strength of the various above-mentioned base materials and an ink television layer.

[0063] In this invention, the secondary particle which has a hydrophilic binder and the mean particle diameter of 30–200nm on a base material is contained in an ink absorptivity layer.

[0064] When the primary particle a hydrophilic binder and whose mean particle diameter are 30–200nm is used on a base material, an opening is not formed in the interior of this particle at all, but in order to secure the amount of openings to need, desiccation thickness increases remarkably, and the coat brittleness mentioned later becomes easy to get worse.

[0065] Moreover, when the secondary particle which has the mean particle diameter exceeding 200nm is used, the glossiness of an opening layer falls and a clear image is no longer obtained.

[0066] It falls or, as for on the other hand using the secondary particle which has the mean particle diameter of less than 30nm, formation of secondary floc with the stable handling nature and stability of the primary particle itself tends to change difficult.

[0067] Although a secondary particle makes the primary particle of the particle size of $1/5 - 1/20$ usually condense and is formed from a secondary particle, it is desirable to make a 3–15nm primary particle condense as a primary particle in this invention here.

[0068] Forming the floc of a secondary particle may make a primary particle condense the 2nd order in which phase that manufactures a record form. Moreover, for example The distributed object of the secondary particle condensed beforehand may be mixed with a hydrophilic binder, and you may apply on a base material. Moreover, a secondary particle may be formed, in case the dispersion liquid of a primary particle are mixed with a hydrophilic binder water solution and coating liquid is prepared. The hydrophilic binder currently distributed in the state of the primary [further] particle may be applied on a base material, and a secondary particle may be formed by heat treatment after a desiccation process or desiccation etc.

[0069] In this invention, the mean particle diameter of a secondary particle says the mean particle diameter of the secondary particle in the opening layer formed on the base material. The mean particle diameter of such a secondary particle observes the cross section and front face of an opening layer with an electron microscope, and is called for as the arithmetic average value (individual number average) in quest of the particle size of the secondary particle of 100 arbitration.

[0070] Here, the particle size of the secondary particle according to individual observes the particle with an electron microscope, measures the area of the projection image, and is called for as a diameter when assuming a circle equal to the area.

[0071] As a particle formed by the secondary condensation which can be used for this invention, although non-subtlety particles, such as a barium sulfate, a calcium carbonate, a zinc oxide, synthetic hectorite, and a silica, etc. are mentioned, especially a silica is desirable.

[0072] When the particle itself tends to condense a silica particle by the hydrogen bond by the surface silanol group and it is made to condense under existence of a hydrophilic binder like especially this invention, comparatively loose condensation (flocculation) is formed and high voidage is attained.

[0073] A silica particle is divided roughly into dry process and a wet method according to a manufacturing method. As a dry-process particle silica, the approach by the gaseous-phase method hydrolysis in the elevated temperature of silicon halide and the approach of carrying out heating hydride generation of silica sand and the corks with an arc process with an electric furnace, and smothering this are learned. Moreover, after the acidolysis of silicate generates active silica as a wet method silica, carry out a polymerization moderately, and it is made to condense and precipitate, and is obtained.

[0074] In the record form of this invention, there is no crack at the time of the film formation nature of a coat, i.e., spreading desiccation of a coat, and a gaseous-phase method silica is the most desirable from the point that a sex with the film is good.

[0075] The alumina denaturation silica processed in part with the alumina in the front face is also contained in the above-mentioned silica.

[0076] moreover, the above — although mean particle diameter can also use together wet method silicas, calcium carbonates, etc., such as colloidal silica which is 3–200nm, in addition to the gaseous-phase method silica used preferably, it is good for especially a gaseous-phase method silica to contain [of all particles] 30 % of the weight or more preferably 20% of the weight or more.

[0077] Although it is desirable in this invention that it is a primary particle with a mean particle diameter of 15nm or less, a primary particle 10nm or less is especially the most desirable from the height of glossiness and voidage.

[0078] There are various approaches in forming the secondary particle which is made to condense the above-

mentioned primary particle and has the mean particle diameter of 30–200nm. For example, change the pH of the dispersion liquid of a uniform primary particle, or once forming the homogeneity coat of an approach and a primary particle which the hydrophilic binder water solution which can consider weak coupling, such as hydrogen bond, as the approach and the particle which add inorganic ion and cause condensation of a particle is added [coat], and makes condensation cause, apply a condensation accelerator, or make it sink in, or there are a method of causing condensation by heat treatment etc., the approach of combining these approaches, etc.

[0079] Moreover, like the above-mentioned, a mixing front with a hydrophilic binder, and after mixing, either after the time of spreading desiccation or desiccation can choose the optimal approach, and can carry out at the formation time of secondary floc.

[0080] In the record form of this invention, as a hydrophilic binder used combining the above-mentioned particle, although polyvinyl alcohol and its derivative, polyalkylene oxide, a polyvinyl pyrrolidone, gelatin, hydroxyl ethyl cellulose, cull BOKIRU methyl cellulose, a pullulan, casein, a dextran, etc. can be used, it is desirable from the point of the film strength immediately after printing that the bloating tendency and the solubility over the high-boiling point organic solvent and water which ink contains use a low hydrophilic binder.

[0081] In especially this invention, polyvinyl alcohol is desirable, and average degree of polymerization is [average degree of polymerization] 2000 or more polyvinyl alcohol most preferably 1000 or more especially. Moreover, especially whenever [saponification / of desirable polyvinyl alcohol / 80 – 100% of] is desirable 70 to 100%.

[0082] Although the particle for forming the opening layer of the record form of this invention and the ratio of a hydrophilic binder may change with the class of hydrophilic binder, the class of particle, the magnitude of the interaction of particle size, a hydrophilic binder, and a non-subtlety particle, etc., generally particles are 4–10 in a weight ratio to a hydrophilic binder.

[0083] When the maximum delivery of the ink in which a ratio exceeds 30 capacity % to the high-boiling point organic solvent in ink especially, and ink exceeds 25ml per two 1m of record forms, as for the ratio of the non-subtlety particle to a hydrophilic binder, 5–10 are desirable at a weight ratio.

[0084] It is desirable to add the hardening agent which can construct a bridge with said hydrophilic binder into the opening layer of the above-mentioned record form at the point of improving the film strength after printing which is amelioration of the film formation nature of an opening layer, the water resisting property of a coat, and the purpose of this invention. Inorganic hardening agents, such as an organic hardening agent which contains an epoxy group, an ethylene imino group, an activity vinyl group, etc. as such a hardening agent, chromium alum, a way acid, or way sand, are mentioned.

[0085] Especially when a hydrophilic binder is polyvinyl alcohol, the epoxy system hardening agent which has at least two epoxy groups in a molecule, a way acid, or way sand is desirable. 1–200mg per above-mentioned binder [hydrophilic] 1g of additions of a hardening agent is 2–100mg preferably.

[0086] Various kinds of additives can be made to contain if needed in the layer of the arbitration by the side of the ink receptiveness layer of the ink jet record form of this invention.

[0087] For example, an ultraviolet ray absorbent given in JP,57-74193,A, a 57-87988 official report, and a 62-261476 official report, JP,57-74192,A, a 57-87989 official report, a 60-72785 official report, The fading inhibitor indicated by a 61-146591 official report, JP,1-95091,A, the 3-13376 official report, etc., An anion, a cation or the various surfactants of Nonion, JP,59-42993,A, The fluorescent brightener indicated by a 59-52689 official report, a 62-280069 official report, a 61-242871 official report, JP,4-219266,A, etc., Various well-known additives, such as lubricant, such as pH regulators, such as a sulfuric acid, a phosphoric acid, a citric acid, a sodium hydroxide, a potassium hydroxide, and potassium carbonate, a defoaming agent, and a diethylene glycol, antiseptics, a thickener, an antistatic agent, and a mat agent, can also be made to contain.

[0088] Into the configuration layer of the arbitration by the side of the ink absorptivity of the record form of this invention, an alkali-metal weak acid salt the poly allylamine of publications, such as the poly cation polyelectrolyte of JP,56-84992,A, a basic latex polymer of JP,57-36692,A, JP,4-15744,B, JP,61-58788,A, and a 62-174184 official report, and given in JP,61-47290,A etc. can be used more than a kind as a deck-watertight-luminaire-ized agent of an image.

[0089] The amount of the spreading solid content by the side of the ink recording surface in the ink jet record form of this invention has in general desirable 5 – 40 g/m², and its 10 – 30 g/m² is more desirable. In addition, from the field of prevention of the curl after record image formation, it is good to form as thinly as possible.

[0090] Moreover, 40 – 80% of the voidage of the ink absorption layer of a record form is desirable. When voidage is less than 40%, in order to secure required void volume, the thickness of an ink absorptivity layer increases too much, and the crack of an ink absorptivity layer and an adhesive property with a base material tend to become a problem. On the other hand, when voidage exceeds 80%, there is an inclination to become easy for the reinforcement of the coat after printing which is the effectiveness of this invention to fall. It is the range whose voidage is 50 – 70% preferably.

[0091] Moreover, although the desiccation thickness of an opening layer is mainly determined by said voidage

and void volume, its 25–55 micrometers are especially more desirable than the viewpoint of crack prevention of a coat 20–60 micrometers.

[0092] Voidage is expressed with the following formulas from the desiccation thickness of void volume and an opening layer here.

[0093] Voidage (%) = $100 \times (\text{void volume (ml/m}^2) / \text{desiccation thickness (micrometer)})$

However, when void volume measures the ink absorptivity layer side of a record form by the approach indicated by the liquid absorptivity test method (Bristow law) of J.TAPPI paper pulp test-method No.51 –87 paper and the paper board by this invention, absorption time amount is expressed with the amount of liquid transition in 2 seconds (ml/m²). In addition, although the liquid used at this time is pure water (ion exchange water), in order to make distinction of measurement area easy, less than 2% of water soluble dye may be contained.

[0094] In order to adhere at the time of piling up immediately after curl prevention or printing to the opposite side and to raise prevention and ink-proof imprint nature further, as for the ink absorptivity layer side of the record form of this invention, it is desirable to prepare the back layer of various classes.

[0095] Although the configuration of a back layer changes also with the class of base material, thickness, and the configuration and thickness of an ink absorptivity layer, generally a hydrophilic binder and a hydrophobic binder are used. The range of the thickness of a back layer is usually 0.1–10 micrometers.

[0096] Moreover, it adheres to a back layer as other record forms, and-izing of the front face can be carried out [split face] to prevention, note nature amelioration, and a pan for conveyance nature amelioration within an ink jet recording device. A well-known particle organic [an organic particle size is 2–20 micrometers], or inorganic is preferably used for this purpose.

[0097] In the ink jet record approach of this invention, the thing of the amount [in / in said void volume which a record form has / the maximum ink discharge quantity] of high-boiling point organic solvents which it has 3 or more times is required.

[0098] Here, the maximum ink discharge quantity is an amount from which the amount of ink breathed out by per two 1m of record forms becomes max in the conditions which say the amount of maximum regurgitation ink at the time of recording the usual full color image, and record the usual image. When the case where, as for this, the maximum concentration of the ink of a specific color is formed according to the ink regurgitation conditions of a recording device becomes the maximum ink discharge quantity, Although there may be various cases when the case where black is formed by further 3 colors when the case where the color formed by some two specific colors is formed becomes a maximum delivery. becomes a maximum delivery It has set to this invention, and even if it is the case of a gap, it is necessary to make it 3 or more times of the amount of openings to the amount of high-boiling point organic solvents in the amount of the maximum ink.

[0099] When the reinforcement of the coat after printing becomes inadequate to the amount of high-boiling point organic solvents in the amount of the maximum ink when the amount of openings is less than 3 times, or paper is piled up, and saved especially by the high-humidity condition, it becomes easy to imprint a color.

[0100] Next, the water-soluble ink used for the ink jet record approach of this invention is explained below.

[0101] The water-soluble ink used for this invention is usually water soluble dye and a solvent object, and a record liquid that consists of other additives. Although water soluble dye, such as direct dye well-known as water soluble dye at an ink jet, acid dye, basic dye, reactive dye, or a food dye, can be used, direct dye or acid dye is desirable.

[0102] Although it becomes as a subject, when liquid ink dries water, in order that a color may deposit and the solvent of water color ink may prevent the blinding in a nozzle tip or an ink supply path, a high-boiling point organic solvent with the boiling point liquefied above about 120 degrees C is usually used at a room temperature. A high-boiling point organic solvent needs to have a high miscibility to water, while it is required that it should have vapor pressure far lower than water, since it has the operation which formed elements, such as a color, deposit and prevents generating of a big and rough sludge when water evaporates.

[0103] such a purpose — as a high-boiling point organic solvent — the organic solvent of a high-boiling point — usually — many — use — now, ** as an example Ethylene glycol, propylene glycol, a diethylene glycol, Triethylene glycol, a glycerol, the JICHIREN glycol monomethyl ether, The diethylene-glycol monobutyl ether, the triethylene glycol monobutyl ether, The glycerol monomethyl ether, 1 and 2, 3-butane triol, 1 and 2, 4-butane triol, Alcohols, such as 1, 2, 4-pentanetriol, 1 and 2, 6-hexane triol, thiodiglycol, triethanolamine, and a polyethylene glycol (average molecular weight is about 300 or less), are mentioned. Moreover, dimethylformamide, N-methyl pyrrolidone, etc. can be used also besides having described above.

[0104] Also in the high-boiling point organic solvent of these many, the low-grade alkyl ether of the polyhydric alcohol of polyhydric alcohol, such as a diethylene glycol, triethanolamine, and a glycerol, and the triethylene glycol monobutyl ether etc. is desirable.

[0105] As an additive of others which water color ink contains, a pH regulator, a sequestering agent, an antifungal agent, a viscosity controlling agent, a surface tension regulator, a wetting agent, a surfactant, a rust-proof, etc. are mentioned, for example.

[0106] In order that the wettability to a record form may make water-color-ink liquid good, it is the purpose which stabilizes the regurgitation from an ink jet nozzle, and in 25 degrees C, it is desirable to have the surface tension of 28 – 40 dyne/cm within the limits preferably 25 to 50 dyne/cm.

[0107] Moreover, the viscosity of water color ink is usually 2.5 – 5cp preferably two to 8 cp in 25 degrees C.

[0108] The range of pH of water color ink is usually 4–10.

[0109] In the ink jet record approach of this invention, since the diameter of the minimum dot with a diameter of about 20–60 micrometers is obtained in the record paper as a minimum liquid ink drop in the case of the capacity of 1–30x10⁻³nl, it is desirable. The color-print printed with such a diameter of a dot gives a high-definition image. It is the case where the drop which has the volume of 2–20x10⁻³nl preferably is breathed out as the minimum drop.

[0110] Moreover, in the method recorded about a Magenta and cyanogen at least in the ink whose concentration is two kinds from which said water-soluble ink differs more than twice respectively, since low-concentration ink is used, it is hard coming to carry out discernment of a dot in the highlights section, but this invention can be applied, also when this recording method is adopted.

[0111] In the ink jet record approach of this invention, as the record approach, various kinds of well-known methods can be used conventionally, and the detail is indicated by the trend (the volume for Koichi Nakamura, March 31, Heisei 7, the Japan science-information incorporated company issue) of for example, an ink jet record technique.

[0112] In the ink jet record approach of this invention, combining suitably approaches, such as making [many / as possible] thickness for the void volume of the record form which lessens the amount of maximum regurgitation ink as much as possible which lowers the ratio in the ink of a high-boiling point organic solvent, the approach of making void volume to the amount of high-boiling point organic solvents in the amount of the maximum ink 3 or more times sets up the optimal conditions, and is chosen.

[0113] In this invention, if the amount of organic solvents which remains in the opening layer after printing exceeds one third of void volume, as described above, the film strength immediately after printing will tend to fall, and will become. Ink with the high content of a high-boiling point organic solvent (for example, ink containing the high-boiling point organic solvent more than 40 capacity %) is used. Although the amount of residual organic solvents needs to create to a sake more [far] void volume than the void volume needed for absorbing ink completely in the case of printing also in the location which carried out the maximum ink regurgitation making it be 1/3 or less [of the amount of openings] In this case, it will be necessary to thicken thickness of an ink absorption layer superfluously, and becomes easy to produce a crack etc. In this invention from this viewpoint, 30% or less is desirable 35% or less by capacity especially as an amount of ink solvents.

[0114] On the other hand, although the minimum of the content of a high-boiling point organic solvent is decided from mainly giving blinding, the optimal viscosity, and surface tension to ink etc., it is desirable to contain more than 15 capacity % preferably more than 10 capacity % mainly from a viewpoint of blinding prevention.

[0115] the solvent whose amount when the high-boiling point organic solvent ratio in ink being expressed with capacity % of the high-boiling point organic solvent which ink contains here, for example, measuring by the high-boiling point organic solvent independent is 10ml — ink 100ml — when contained in inside, it should display as 10% Moreover, when a high-boiling point organic solvent is two or more kinds, the ratio of each high-boiling point organic solvent is added and expressed.

[0116] The most effective approach of lessening the amount of maximum regurgitation ink as much as possible is making the diameter of a dot as small as possible. In order to lose the white omission of the maximum concentration region, the number of dots per unit area increases, as the diameter of a dot becomes small, but the capacity per dot decreases conversely, and since there is more this reduction than the increment in the number of dots, the amount of ink to a record form usually decreases. Consequently, the thickness needed as void volume is also mitigated.

[0117] Therefore, since the amount of ink printed by the record form decreases with reduction of the diameter of a dot, it is desirable that the diameter at the maximum equator (diameter when assuming a circle equal to this in quest of the dot area when a single dot is printed in monochrome ink) of the dot used in this invention in a maximum-density region sets 80 micrometers or less especially to 60 micrometers.

[0118] Furthermore, that it is easy to cause a crack by the impact from the outside etc. with under the handling at the time of, as for thickness becoming carelessly and thick although the effectiveness of this invention is easy to be acquired the more the more there is much void volume, the brittleness of a coat deteriorating, and being a desiccation process at the time of manufacture, or it being damp, and saving, other papers, a writing implement, etc., it becomes, or an adhesive property with a base material tends [further] to fall, and it becomes. Especially, as for the crack at the time of manufacture, it is desirable to make desiccation thickness of a coat as thin as possible in many cases with the fall of gloss, since the effect on image quality is also comparatively large.

[0119] As mentioned above, as mentioned above, 40 to 80%, the voidage of a coat is 50 – 70% preferably, and it

is most desirable to make it void volume become the 3 to 4 times as much range as the amount of high-boiling point organic solvents at the time of the maximum ink regurgitation. Especially use of the hardening agent which constructs a bridge in the hydrophilic binder of a coat for this purpose is desirable.

[0120]

[Example] Although the example of this invention is given and explained below, this invention is not limited to these examples.

[0121] It was obtained by the gaseous-phase method example 1 mean particle diameter is about 7nm, and 150g of primary particle silica powder was added in 1000ml of pure water, the high-speed homogenizer distributed, and pale clear dispersion liquid were obtained. Next, in this silica water dispersion (I), average degree of polymerization added gradually 2% polyvinyl alcohol water-solution (II) (ethyl acetate is contained for surface active agent -1 8% of the weight 0.1% of the weight) 1250ml whenever [saponification / whose] is 88% by 3500. Subsequently, 20ml of 4% way sand water solutions was added as a hardening agent, the high-speed homogenizer distributed, and white translucent-like coating liquid was obtained (this liquid is 6 times in a weight ratio to polyvinyl alcohol about a silica).

[0122] Next, the paper base material which covered both sides of the stencil paper of 170g/m² with polyethylene (an anatase mold titanium dioxide is contained 13% of the weight in the polyethylene layer by the side of 240 micrometers in thickness, and a recording surface.) the back layer which makes solid content Tg=65 degree C acrylic latex resin at a rear-face side, and is contained two times 0.3 g/m by making into a mat agent the silica 0.6 g/m² and whose mean diameter are about 13 micrometers — having — it prepared.

[0123] For 95.2% and surface glossiness (75-degree specular gloss), the opacity of the above-mentioned polyethylene covering paper is 2.5mm of criteria length about the wave filtration waviness curve drawn on with a cut-off value [of 0.8mm] acquired from the cross-section curve when measuring the field by the side of an ink absorption layer 90.3% according to JIS-B-0610 conditions. wave filtration max — 100 point of measurement of the arbitration when measuring a wave — max — the number of points 6 micrometers or more was [the wave] one, and the ten-point average of roughness height of the Beck smoothness of the field by the side of 1.3 micrometers and an ink absorption layer was 2100 seconds.

[0124] The 40-degree C coating liquid obtained as mentioned above was applied to the recording surface side of the above-mentioned polyethylene covering paper, and was made to once cool so that spreading coat temperature may turn to 15 degrees C or less (for 20 seconds). Subsequently, the 25-degree C wind was sprayed for the 20-degree C wind for 30 seconds, for 60 seconds and a 45 more-degree C wind were sprayed for 30 seconds and for a 35-degree C wind one by one for 120 seconds, it dried, 25 more degrees C and the ambient atmosphere of 50% of relative humidity were passed for 30 seconds, gas conditioning was carried out, and the record form -1 was produced.

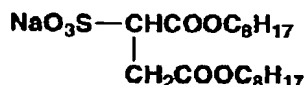
[0125] Next, in the record form -1, the silica was changed into the thing and the 20nm thing whose primary particle size is 13nm, and the record form -2 and the record form -3 as well as the record form -1 were produced.

[0126] The record form obtained as mentioned above was saved for five days at 38 degrees C and 40 - 60% of relative humidity.

[0127]

[Formula 1]

界面活性剤-1



[0128] The above-mentioned record form - About each of 1-3, the mean particle diameter of desiccation thickness and a secondary particle, void volume, and glossiness were measured, and the result shown in Table 1 was obtained.

[0129] In addition, the mean particle diameter of a secondary particle observed the front face of each record form with the electron microscope, asked for the particle size of each particle as a diameter when assuming a circle equal to the area in quest of the projected area about 100 particles of the arbitration of each record form, respectively, and asked for the mean particle diameter of the secondary particle of each record form as an arithmetic average of the particle size of 100 particles.

[0130] Moreover, the Kumagaya Riki Kogyo K.K. make and a Bristow testing-machine II mold (pressure type) were used for void volume, and it calculated the amount of transition for [contact time] 2 seconds as void volume.

[0131] Glossiness measured the specular gloss 75 degrees with the deflection photometer (VGS-101DP) by Nippon Denshoku Industries Co., Ltd.

[0132] On the other hand, the ink of the following presentations was adjusted as an object for ink jet recording

ink -1.

[0133] [Recording ink -1]

Yellow ink Y-1 (high-boiling point organic-solvent ratio: 19.7%)

C. I. direct yellow 86 2.1g Diethylene glycol 15.3ml Glycerol 4.4ml 100ml is made with pure water (ion exchange water).

[0134]

Magenta ink M-1 (high-boiling point organic-solvent ratio: 21.2%)

The following Magenta color -1 1.8g Diethylene glycol 13.1ml Glycerol 8.1ml 100ml is made with pure water (ion exchange water).

[0135]

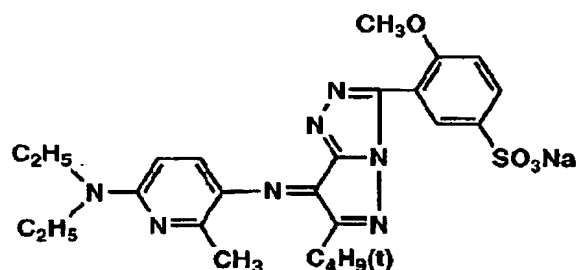
Cyanogen ink C-1 (high-boiling point organic-solvent ratio: 20.3%)

C. I. direct blue 199 2.8g Diethylene glycol 13.1ml Glycerol 7.2ml 100ml is made with pure water (ion exchange water).

[0136]

[Formula 2]

マゼンタ染料-1



[0137] the above-mentioned liquid ink was used and ink jet record of the regurgitation consistency was carried out by 720dpi (regurgitation spacing = about 35 micrometers) record form-1-3 by the on-demand mold ink jet recording head (diameter = of nozzle 25 micrometer, and each ink — drop diameter = — about [about 27 micrometers and / drop volume =] — regurgitation conditions were adjusted, respectively so that it might be set to 10x10-6 microl.) which makes ink breathe out with a piezo trembler. The amounts of maximum regurgitation ink at this time were about 8.1 ml/m2 per ink 1 color. The amount when carrying out the maximum regurgitation of yellow, a Magenta, and the cyanogen ink to coincidence is 24.3 ml/m2.

[0138] The above-mentioned record form - The following approaches estimated the film strength after drying and printing using 1-3, and ink jet recording ink.

[0139] (1) After saving [in coincidence] each color of yellow, a Magenta, and cyanogen for 30 minutes after printing on the highest regurgitation conditions with the drying above-mentioned ink jet printer at 23 degrees C and 65% of relative humidity, the paper of fine quality of 80 g/m2 was saved in piles 200 sheets one whole day and night, and ink imprint nature was investigated on the following criteria.

[0140]

O : — completely — imprint-less O: — although the marks of an imprint of a color remain slightly, the image itself is hardly changeful — **:imprint trace is large, the adhesion of x:paper and an ink absorptivity layer from which a front face will be in a devitrification condition is large, and an image cannot remove paper finely, either — after printing, after saving on the same conditions for 24 hours, the same evaluation was also doubled in piles and paper was performed again.

[0141] (2) After leaving it for after [solid printing] two days of 3 color coincidence on the same conditions as drying evaluation of the film strength after printing (1), the continuation load (0-100g) be applied to the sapphire needle whose tip be 0.3mm in 23 degrees C and the environment of 80% of relative humidity using the **** strength test machine (Hayden try BOGIA, new east science incorporated company make), the film strength be examined, and it asked for the reinforcement by which a coat be destroy as a film strength.

[0142] If it is 30g or more in general by this evaluation approach, it can be said that it has the practically sufficiently high film strength.

[0143] The above-mentioned result is shown in Table 1.

[0144]

[Table 1]

記録用紙	2次粒子粒径	乾燥膜厚 (μm)	空隙容量 (nl/m^2)	空隙率 (%)	V/H	光沢度	乾 燥 性		印字後 皮膜強度
							30分後	24時間後	
1 (本発明)	60 μm	40	25.2	63	5.0	69%	◎	◎	90 g
2 (本発明)	140 μm	41	24.7	60	4.9	52%	◎	◎	>100 g
3 (比較例)	230 μm	42	25.4	60	5.1	14%	◎	◎	>100 g

V/H ; 最大インク吐出時高沸点有機溶媒量 (5.0ml) に対する空隙容量比率 (%)

[0145] Secondary floc is a record form although glossiness is falling greatly exceeding [when the record form -3 is used from the result shown in Table 1] 200nm. - Each of 1 and 2 has high glossiness. It turns out especially that it has high glossiness in the record form -1 whose particle size of a secondary particle is 100nm or less.

[0146] On the other hand, it is a record form. - In 1-3, in ink jet record of this example, each has the 4.9 to 5.1 times as many opening as this to V/H of high-boiling point organic solvents, i.e., the amount at the time of the maximum ink regurgitation, and it has drying [good].

[0147] As mentioned above, record form - If the record approach of this invention using 1 and 2 is followed, it turns out that it is compatible in the high film strength after high glossiness, drying [good], and printing.

[0148] The ink jet recording ink -1 used in the example 2 example 1 is changed into the following recording ink - 2, the amount of drops breathed out from a head is adjusted so that it may become the same amount as an example 1, and it is a record form. - The result which evaluates the film strength after drying and printing like an example 1 using 1-3, and is shown in Table 2 was obtained.

[0149] [Recording ink -2]

Yellow ink Y-2 (high-boiling point organic-solvent ratio: 26.3%)

C. I. direct yellow 86 2.1g Diethylene glycol 22.3ml Glycerol 4.0ml 100ml is made with pure water (ion exchange water).

[0150]

Magenta ink M-2 (high-boiling point organic-solvent ratio: 29.8%)

Magenta color -1 1.8g Diethylene glycol 22.0ml Glycerol 7.8ml 100ml is made with pure water (ion exchange water).

[0151]

Cyanogen ink C-2 (high-boiling point organic-solvent ratio: 29.7%)

C. I. direct blue 199 2.8g Diethylene glycol 24.6ml Glycerol 5.1ml 100ml is made with pure water (ion exchange water).

[0152]

[Table 2]

記録用紙	V/H	乾 燥 性		印字後 皮膜強度
		30分後	24時間後	
1 (本発明)	3.6	◎	◎	60 g
2 (本発明)	3.5	◎	◎	70 g
3 (比較例)	3.6	◎	◎	80 g

V/H ; 最大インク吐出時高沸点有機溶媒量 (7.0ml) に対する空隙容量比率 (%)

[0153] It is a record form, even if it makes the amount of ink solvents increase and void volume falls to about 3.5 to 3.6 times of the high-boiling point organic solvent at the time of the maximum ink regurgitation from the result shown in Table 2. - If the record approach of this invention using 1 and 2 is followed, although the film strength immediately after printing will fall a little rather than an example 1, it is in the level which should be satisfied enough practically.

[0154] The ink jet recording ink -1 used in the example of comparison -1 example 1 is changed into the following recording ink -3, the amount of drops breathed out from a head is adjusted so that it may become the same amount as an example 1, and it is a record form. - The result which evaluates the film strength after drying and printing like an example 1 using 1-3, and is shown in Table 3 was obtained.

[0155] [Recording ink -3]

Yellow ink Y-3 (high-boiling point organic-solvent ratio: 36.4%)

C. I. direct yellow 86 2.1g Diethylene glycol 31.8ml Glycerol 4.6ml 100ml is made with pure water (ion exchange water).

[0156]

Magenta ink M-3 (high-boiling point organic-solvent ratio: 37.8%)

Magenta color -1 1.8g Diethylene glycol 32.6ml Glycerol 5.2ml 100ml is made with pure water (ion exchange water).

[0157]

Cyanogen ink C-3 (high-boiling point organic-solvent ratio: 37.2%)

C. I. direct blue 199 2.8g Diethylene glycol 31.3ml Glycerol 5.9ml 100ml is made with pure water (ion exchange water).

[0158]

[Table 3]

記録用紙	V/H	乾燥性		印字後 皮膜強度
		30分後	24時間後	
1 (比較例)	2.8	×	△	20 g
2 (比較例)	2.7	×	△	25 g
3 (比較例)	2.8	△	△	30 g

V/H: 最大インク吐出時高沸点有機溶媒量 (9.0ml) に対する
空隙容量比率 (%)

[0159] This example of a comparison is a record form although it is the case where it is made 3 or less times to the high-boiling point organic solvent at the time of the maximum ink regurgitation. - Both 1-3 are known by that drying falls more greatly than examples 1 and 2, and is in the level from which the film strength after printing also gets worse in the high record form of especially glossiness, and may produce a problem practically.

[0160] Record form produced in the example 3 example 1 - Humid thickness is made to increase by about 20% in 1-3 using each coating liquid, respectively, and it is a record form. - It is a record form like 1-3. - 1A, 2A, and 3A were produced.

[0161] Secondary particle particle size, desiccation thickness, void volume, and glossiness were measured like the example 1.

[0162] Ink jet record was performed using the recording ink which, on the other hand, used the ink JIETO recording apparatus used in the example 1, and was used in the example 1 of a comparison as recording ink, and the film strength after drying and printing was investigated like the example 1. A result is shown in Table 4.

[0163]

[Table 4]

記録用紙	2次粒子径	乾燥膜厚 (μm)	空隙容量 (ml/m^2)	空隙率 (%)	V/H	光沢度	乾燥性		印字後 皮膜強度
							30分後	24時間後	
1 A (本発明)	60 μm	48	30.2	63	3.4	64%	◎	◎	50 g
2 A (本発明)	140 μm	48	30.5	63	3.4	50%	◎	◎	60 g
3 A (比較例)	230 μm	49	30.1	61	3.3	10%	◎	◎	60 g

V/H: 最大インク吐出時高沸点有機溶媒量 (9.0ml) に対する空隙容量比率 (%)

[0164] Although desiccation thickness and void volume increase in proportion [almost] to humid thickness by increasing the humid thickness at the time of spreading from Table 4, there is an inclination for glossiness to fall a little.

[0165] This will be because the crack of the letter of a crack slight on the front face of an ink absorptivity layer has arisen at the time of spreading desiccation, if it sees in a detail.

[0166] Record form whose mean particle diameter of a secondary particle the film strength after drying [good]

and printing is maintained when the amount of openings of a record form exceeds 3 times of the amount of high-boiling point organic solvents at the time of the maximum ink regurgitation, and is moreover 200nm or less even if it is the case where the ink which contains a high-boiling point organic solvent by high concentration from the result of Table 4 is used – When 1 and 2 are used, it turns out that high glossiness is also attained.

[0167] In the ink JIETO recording apparatus used in the example of comparison 2 example 1, regurgitation conditions were changed into the head adjusted, respectively so that the diameter of a drop by which diameter = of nozzle 30 micrometer and each ink are breathed out might be set to about 32 micrometers and drop volume = abbreviation 18x10⁻⁶ microl in an ink jet recording head (recording ink used what was used in the example 3). Moreover, record form which used the regurgitation consistency in the example 3 by 600dpi (regurgitation spacing **42 micrometer) – Ink jet record was carried out at 1A-3A. The amounts of maximum regurgitation ink at this time were about 10.2 ml/m² per ink 1 color. The amount when carrying out the maximum regurgitation of yellow, a Magenta, and the cyanogen ink to coincidence is 30.6 ml/m².

[0168] The film strength after drying and printing was evaluated like the example 1, and the result shown in Table 5 was obtained.

[0169]

[Table 5]

記録用紙	空隙容量	V/H	乾 燥 性		印字後 皮膜強度
			30分後	24時間後	
1 A (比較例)	30.2	2.7	×	△	15 g
2 A (比較例)	30.5	2.7	×	△	20 g
3 A (比較例)	30.1	2.7	△	○	25 g

V/H : 最大インク吐出時高沸点有機溶媒量 (11.3ml) に対する空隙容量比率 (%)

[0170] Moreover, since the discharge quantity as [whole] a record form increased even if it made regurgitation spacing correspond to this and the amount of openings became 3 or less times according to increase of the diameter of a drop to the amount of high-boiling point organic solvents at the time of the maximum ink regurgitation even if it used the record form and recording ink which were used in the example 3 from the result of Table 5, the film strength after drying and printing fell.

[0171] Record form produced in the example 4 example 1 – Record form to which each humid thickness was made to increase by about 40% in 1-3 – It is a record form about 1B-3B. – It produced like 1-3.

[0172] Record form – The result of the particle size of the secondary particle of 1B, 2B, and 3B, void volume, and glossiness is shown in Table 6.

[0173] Furthermore, the ink jet recording device used in the example 2 of a comparison estimated it the example 2 of a comparison similarly using the recording ink used in the example 1 of a comparison, and the result shown in Table 6 was obtained.

[0174]

[Table 6]

記録用紙	2次粒子粒径	乾燥膜厚 (μm)	空隙容量 (ml/m ²)	空隙率 (%)	V/H	光沢度	乾 燥 性		印字後 皮膜強度
							30分後	24時間後	
1 B (本発明)	60 μm	55	35.4	64	3.1	56%	○	◎	40 g
2 B (本発明)	140 μm	56	35.8	64	3.2	42%	○	◎	50 g
3 B (比較例)	240 μm	56	35.6	64	3.2	9%	○	◎	60 g

V/H : 最大インク吐出時高沸点有機溶媒量 (11.3ml) に対する空隙容量比率 (%)

[0175] From the result of Table 6, although the amount of openings increases according to the further increase of spreading thickness, glossiness falls further. However, record form – If it is 1B and 2B extent, although it is in the level which can be permitted somehow practically, the gloss of 3B is extinguished completely and has become the so-called mat side.

[0176] Moreover, if the film strength after drying or printing is measured against examples 1 and 2, although it will fall from the result of Table 6, the good result is shown if compared with the examples 1 and 2 of a comparison.

[0177] Record form produced in the example 5 example 1 – Record form which does not add way sand as a hardening agent in 1-3 – 1C, 2C, and 3C were produced.

[0178] It is a record form except having changed the polyvinyl alcohol concentration of a water solution (II) to 4% in the record form produced in the example 1. – Record form-1D 2D and 3D were produced like 1-3

[0179] Record form produced in the example 1 – It is a record form except average degree of polymerization having changed polyvinyl alcohol into the polyvinyl alcohol whenever [saponification / whose] is 88% in about 1700 in 1–3. – It is a record form like 1–3. – 1E, 2E, and 3E were produced.

[0180] Moreover, record form produced in the example 1 – In 1–3, a 70–100-degree C wind is sprayed, and it dries, without cooling after applying in the polyethylene covering paper at the time of desiccation, and is a record form. – 1F, 2F, and 3F were produced.

[0181] Desiccation thickness, void volume, and glossiness were investigated for each above-mentioned record form like the example 1. A result is shown in Table 7.

[0182] On the other hand, the film strength after drying and printing was investigated like the example 2 using the recording ink used in the example 2. A result is shown in Table 7.

[0183]

[Table 7]

記録用紙	2次粒子粒径	乾燥膜厚 (μm)	空隙容量 (ml/m^2)	空隙率 (%)	V/H	光沢度	乾燥性		印字後 皮膜強度
							30分後	24時間後	
1 C (本発明)	60 μm	41	24.4	59	3.5	61%	◎	◎	50 g
2 C (本発明)	140 μm	42	24.0	57	3.4	49%	◎	◎	50 g
3 C (比較例)	230 μm	41	24.7	60	3.5	11%	◎	◎	60 g
1 D (比較例)	50 μm	37	17.9	48	2.6	73%	×	△	10 g
2 D (比較例)	130 μm	38	18.3	48	2.6	59%	×	△	10 g
3 D (比較例)	220 μm	37	18.4	50	2.6	36%	×	△	20 g
1 E (本発明)	60 μm	40	24.6	62	3.5	55%	◎	◎	60 g
2 E (本発明)	140 μm	41	25.7	63	3.7	43%	◎	◎	80 g
3 E (比較例)	230 μm	41	25.9	63	3.7	8%	◎	◎	>100 g
1 F (比較例)	60 μm	35	17.8	51	2.5	51%	×	△	10 g
2 F (比較例)	140 μm	36	18.3	51	2.6	40%	×	△	10 g
3 F (比較例)	230 μm	36	19.5	54	2.8	10%	×	○	30 g

V/H ; 最大インク吐出時高沸点有機溶媒量 (7.0ml) に対する空隙容量比率 (%)

[0184] It is a record form when way sand is removed as a hardening agent from the result of Table 7 (record form – 1C–3C). – Although the film strength after printing and glossiness are falling a little as compared with 1–3, void volume and drying hardly change.

[0185] Although glossiness improves when the amount of the polyvinyl alcohol used is doubled in the record form –1 and the ratio of the hydrophilic binder to a non-subtlety particle is lowered to one half, about 2/of void volume is set to 3, the void volume to the amount of high-boiling point organic solvents becomes 3 or less times, and the film strength after drying or printing is falling greatly.

[0186] In the record form –1, although glossiness is ***** (ing) when polyvinyl alcohol is changed into the lower thing of average degree of polymerization, when way sand is removed in general, it has drying [near] and a near film strength.

[0187] Drying and a film strength not only got worse, but by the sample which carried out stoving, without cooling after applying in the case of manufacture of the record form –1, and making it set, void volume fell and the glossy fall accompanying a crack was accepted.

[0188]

[Effect of the Invention] As mentioned above, if the ink jet record approach of this invention is used, it will have high maximum density and high visibility, and a highly-glossy high-definition color picture will be obtained. Moreover, the full color image in which the reinforcement of a surface coat is sufficiently strong and handling nature was excellent immediately after printing is obtained.

[Translation done.]

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TECHNICAL FIELD

[Field of the Invention] This invention relates to the ink jet record approach of could record the color picture which has a high-class feeling by high definition without high glossiness and nonuniformity especially about the color ink jet record approach which records using water color ink, and having improved the handling nature immediately after record.

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PRIOR ART

[Description of the Prior Art] although ink jet record makes the minute drop of ink fly by various working principles, and is made to adhere to record sheets, such as paper, and an image, an alphabetic character, etc. are recorded, a high speed, the low noise, and multiple-color-izing are comparatively easy — etc. — it has the advantage. About the blinding of a nozzle and the maintenance which had become a problem from the former by this method, from both sides of ink and equipment, amelioration progresses and it has spread through various fields, such as various printers, facsimile, and a computer terminal, quickly in current.

[0003] The detail is indicated by the trend (the volume for Koichi Nakamura, March 31, Heisei 7, the Japan science-information incorporated company issue) of for example, an ink jet record technique.

[0004] As a record form used by this ink jet recording method, also when a printing dot laps [that a color tone is brightly skillful and absorption of ink] early, the diffusion to the longitudinal direction of ink flowing out or not spreading and a printing dot is not large [the concentration of a printing dot is high, and] beyond the need, and generally it is required that the circumference should be smooth and should not fade etc.

[0005] By the way, many attempts which are going to bring the image quality acquired by color ink jet record close to a photograph are performed in recent years.

[0006] This is roughly divided into the property related to an ink absorptivity layer, the property about amelioration of the image quality resulting from the dot formed in a record form, and the property related to a base material.

[0007] Or it raises the smooth nature on the front face of ink which raises the transparency of an ink absorptivity layer and improves printing concentration as an attempt which improves an ink absorptivity layer and raises glossiness, the maximum ink absorption capacity is secured enough, it is making it ink not overflow in a maximum-density region, and the extensive amelioration technique has been proposed from the former.

[0008] on the other hand, the greatest point of the improvement in image quality resulting from a dot be that one one piece dot prevent from identify visually, therefore it be the point to form a liquid ink drop into a small drop, to use low-concentration ink together as color concentration, in order that discernment of the dot in the highlights section may carry out as [be / difficult] especially, etc., and in order to improve this point, various amelioration techniques have be propose from the former.

[0009] Moreover, in the regular paper and paper of fine quality with which ink tends [comparatively] to permeate as a record form or the usual art paper, or the comparatively big cast coated paper of absorptivity, since ink permeates into a base material, a wrinkling occurs after record only in the printing section, and print quality is reduced greatly. Moreover, since ink permeates into paper fiber or permeates into an opaque high white-pigments content coat layer, there is a fault from which a clear image is hard to be obtained that it is hard to come out of maximum density.

[0010] Furthermore, since the white pigments of paper fiber or comparatively big size exist [the roundness of a dot], it is also the cause of degradation of the image quality at the time of turbulence and this carrying out ink jet record.

[0011] In order to acquire image quality with a high-class feeling like a photograph as an ink jet record form from the above point, For example, the base material for photographs with which water color ink cannot permeate easily, the record form (it Bulletein(s) (Vol.21, NO. 1978 [6 or], 2502 pages) for example, IBM Technical Disclosure [] —) which applied the ink absorptivity layer on the paper base material for the photographs which covered especially both sides with polyolefine U.S. Pat. No. 3,889,270, JP,7-179032,A, 7-179025, And it is indicated by 7-32723 and the 8-174992 official report, the record form (for example, indicated by JP,61-135783,A) which applied the ink absorptivity layer on white plastic film is used increasingly preferably.

[0012] By the way, in order to attain the image quality of the above-mentioned photograph average, it is, Although it is that especially the thing established for an ink absorptivity layer with comparatively high transparency on the base material of low ink absorptivity is desirable, when the front face of an ink absorptivity layer mat-izes, and carries out a gloss fall or the ink absorption layer itself has the quite big microstructure, the opacity of an ink absorptivity layer goes up in addition to the fall of gloss, and it is hard to attain about the same image quality as a photograph in many cases.

[0013] Although many things are known from the former as an ink absorptivity layer prepared on a base material, it is roughly classified into two types.

[0014] One of them is the ink absorptivity layer of a swelling mold, and it is an ink absorptivity layer which makes a hydrophilic binder a subject. As for this, a liquid ink drop evaporates the moisture of a hydrophilic binder which holds temporarily mainly according to a swelling operation, and ink contains gradually after printing, and a high-boiling point organic solvent.

[0015] The advantage of the swelling mold record form which prepared this ink absorptivity layer on the base material is in the point that very high glossiness and high maximum density are obtained, after an ink solvent (water and high-boiling point organic solvent) evaporates completely. On the other hand, this swelling mold record form is late compared with the opening mold record form which ink rate of absorption mentions later, there is a problem to which beading etc. is cause in a high ink field and image quality tends to fall, and there is a problem accompanying be put on the damp or wet condition which the hydrophilic binder swelled for a while since evaporation of an ink solvent, especially a high-boiling point organic solvent is still very slower, after print for a long period of time. Specifically, it is in the situation that a printing front face cannot be strongly ground for several days by the case for several after [printing] hours, or paper etc. cannot be piled up.

[0016] As an ink absorptivity layer of a mold other than the above-mentioned swelling mold, there is an opening mold record form with which an ink absorptivity layer has opening structure. By holding ink temporarily to this opening in the case of ink jet record, this record form absorbs ink and there is [in / in ink rate of absorption / a high ink field] little degradation of image quality early compared with a swelling mold.

[0017] Moreover, though the organic solvent remained in opening structure when this kind of ink absorptivity layer had void volume of enough to the amount of ink, at least, a front face will be seemingly got dry immediately after printing, a front face is touched or it becomes once possible to pile up prints etc.

[0018] Especially the silica particle that a particle with a particle size small moreover (especially 200nm or less is desirable) is preferably used from the point that a layer with comparatively high transparency is formed, as this kind of an ink absorptivity layer with a low refractive index (about 1.6 or less refractive index is especially desirable), and fulfills these conditions especially is desirable.

[0019] As a conventional technique which uses such a particle silica for an ink JEITO record form, JP,3-56552,B is made to condense the secondary particle silica obtained by the gaseous-phase method primary particle size is 10-30nm, and the record form which has the ink absorption layer which the surface area by the BET adsorption method makes form the particle which is 80-200m²/g, and contains is indicated.

[0020] Moreover, for said JP,8-174992,A, a mean diameter uses a non-subtlety particle and a hydrophilic binder 10nm or less on a polyolefine covering paper base material, and the ink jet record form which obtains high glossiness is indicated.

[0021] However, the inclination for the physical reinforcement of surface glossiness and the front face after printing to conflict in the case of the ink absorptivity layer which has opening structure is large.

[0022] That is, although it will be hard to produce the problem referred to as that ink imprints it even if the reinforcement of the front face after printing is good, and it touches a front face or it piles up paper etc. if the magnitude and the micro opening structure of a particle which are contained there exceed 200 micrometers when an opening layer is seen in micro, the inclination for glossiness to fall extremely is large.

[0023] Moreover, if the magnitude and the micro opening structure of a particle are set to 200nm or less, although gloss will improve gradually, the trace becomes easy to remain, when the softness of the front face after printing increases, the sample was piled up, an ink imprint begins to take place partially or paper is written to an ink absorption stratification plane side with a pencil etc. from on the in piles. This problem will become still larger if especially opening structure is set to 100nm or less.

[0024] If the softness of the front face immediately after this printing is compared with the surface state of the aforementioned swelling mold ink absorptivity layer, it is in the level expected amelioration of a far good thing.

[0025] Although the time amount to which the moisture itself remains in an opening layer although moisture and a high-boiling point organic solvent are one of causes of the problem related to the reinforcement of the coat after such printing cannot become the problem that such a problem is not much big, comparatively easily because of a short time, generally evaporation of a high-boiling point organic solvent tends to receive constraint in handling nature in the meantime, in order for a room temperature to take the time amount of several days.

[0026] When the print after printing is saved with a high-humidity state, since more many moisture is maintained by the coat, this problem tends to change notably. Moreover, this problem tends to arise in the part by which the peak of the amount of ink was breathed out.

[0027] It is presumed that it is because the structure of a coat became is easier to be destroyed by the force applied from the outside when a touch area with the paper which the irregularity of the front face of an ink absorptivity layer becomes small one, and is piled up although the reason of why becoming easy to produce this problem when opening structure is set to 200nm or less is not certain becoming large, and opening structure made it detailed.

[0028] Although the record form which used this particle silica has comparatively high ink absorptivity and glossiness, the solution over the above mentioned technical problem is not given to said JP,8-174992,A and JP,3-56552,B.

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EFFECT OF THE INVENTION

[Effect of the Invention] As mentioned above, if the ink jet record approach of this invention is used, it will have high maximum density and high visibility, and a highly-glossy high-definition color picture will be obtained. Moreover, the full color image in which the reinforcement of a surface coat is sufficiently strong and handling nature was excellent immediately after printing is obtained.

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] The technical problem which this invention is made in view of the above-mentioned actual condition, and this invention tends to solve is to offer the ink jet record approach of having reconciled high-glossiness, drying [with the early coat after printing], and a good physical property, in case water color ink is used for the ink jet record form which has the ink absorptivity layer which consists of opening structure on a low absorptivity base material and ink jet record is carried out.

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MEANS

[Means for Solving the Problem] In the ink jet record approach which records at least the technical problem which above-mentioned this invention tends to solve in yellow, a Magenta, and the water-soluble ink of cyanogen on the record form which has an ink absorptivity layer on a non-absorptivity base material These record forms are a hydrophilic binder and an ink jet record form which has an opening layer containing the secondary particle which has a 30-200nm mean diameter. It is attained by the ink jet record approach characterized by the void volume of this opening layer being 3 or more times of the volume of the high-boiling point organic solvent which ink in case ink discharge quantity is max contains.

[0031] This invention is explained to a detail below.

[0032] As a non-absorptivity base material used for the record form of this invention, the paper base material which covered plastic film and both sides with polyolefine is used preferably.

[0033] As a plastic film base material, plastic film base materials, such as polyethylene, polypropylene, polystyrene, polyethylene terephthalate, polyethylenenaphthalate, triacetyl cellulose, a polyvinyl chloride, polyimide, a polycarbonate, and cellophane, etc. are desirable, for example.

[0034] These plastic film can use suitably a transparent thing, a translucent thing, and an opaque thing properly according to an application.

[0035] When considering as a white film, you may be the base material which prepared the layer which may use the base material which the plastic film base material was made to contain white pigments, such as a small amount of barium sulfate, titanium oxide, and a zinc oxide, and was obtained as it is, and has white pigments (titanium oxide, barium sulfate, etc.) in the side near the base material by the side of the rear face of a transparent film base material, or an ink absorptivity layer.

[0036] Moreover, the paper base material which covered both sides with the polyethylene usually conventionally used in color printing paper as a paper base material which covered both sides with polyolefine is desirable. In this case, it is desirable to make the titanium oxide of an anatase mold or a rutile mold contain three to 20% of the weight to polyethylene in the polyethylene resin layer by the side of an ink absorptivity layer from there not being even improvement in the opacity of a base material or a whiteness degree or a fall of the sharp nature of an image obtained.

[0037] In this invention, a white film base material or the paper base material which covered both sides with polyolefines, such as polyethylene, is desirable, and the paper base material which covered both sides with the polyolefine which has a high-class feeling especially by low cost is the most desirable than the viewpoint which obtains a high-definition color picture.

[0038] Hereafter, especially the paper base material that covered both sides with the polyethylene used preferably is explained.

[0039] The stencil paper used for a paper base material uses wood pulp as the main raw material, and, in addition to wood pulp, paper making is carried out using synthetic fibers, such as synthetic pulps, such as polypropylene, or nylon, and polyester, if needed. Although both LBKP, LBSP, NBKP, NBSP LDP and NDP LUKP and NUKP can be used as wood pulp, it is desirable to use more many [for a staple fiber] LBKP, NBSP(s), LBSP(s), and NDP (s) and LDP(s). However, it reaches LBSP or the ratio of LDP has 10 % of the weight or more and 70 desirable % of the weight or less.

[0040] The pulp of the above-mentioned pulp which chemical pulp with few impurities (sulfate pulp and sulfite pulp) was used preferably, and performed bleaching processing, and raised the whiteness degree is also useful.

[0041] Hara Kaminaka can add suitably flexible-ized agents, such as moisture hold-back agents, such as paper reinforcing agents, such as white pigments, such as sizing compounds, such as a higher fatty acid and an alkyl ketene dimer, a calcium carbonate, talc, and titanium oxide, starch, polyacrylamide, and polyvinyl alcohol, a fluorescent brightener, and polyethylene glycols, a dispersant, and the 4th class ammonium, etc.

[0042] The freshness of the pulp used for paper making has desirable 200-500 cc by convention of CSF, and 30 thru/or 70% have the desirable sum of 24-mesh residue weight % and weight % for 42-mesh ** as which the fiber length after beating is specified to JIS-P -8207. In addition, as for weight % of the four-mesh residue, it is desirable that it is 20 or less % of the weight.

[0043] The basis weight of stencil paper has 60 thru/or desirable 250g, and 90 thru/or especially its 200g are desirable. The thickness of stencil paper has 50 thru/or desirable 250 micrometers.

[0044] After a paper-making phase or paper making, calender processing of the stencil paper can be carried out, and it can also give the Takahira slippage. A stencil paper consistency has 0.7 thru/or common 1.2 g/m² (JIS-P-8118). Furthermore, stencil paper stiffness has 20 thru/or desirable 200g on the conditions specified to JIS-P-8143.

[0045] A surface sizing compound may be applied to a stencil paper front face, and the sizing compound which can be added to said Hara Kaminaka as a surface sizing compound, and the same sizing compound can be used.

[0046] When pH of stencil paper is measured by the hot water extraction method specified by JIS-P-8113, mainly although the polyethylene with which that it is 5-9 cover a desirable stencil paper front face and a desirable rear face is the polyethylene (LDPE) of a low consistency, and/or polyethylene (HDPE) of high density, a part of other LLDPE(s), polypropylene, etc. can be used for it.

[0047] As for especially the polyethylene layer by the side of an ink absorbing layer, what added the titanium oxide of a rutile or an anatase mold in polyethylene as widely performed by the printing paper for photographs, and improved opacity and a whiteness degree is desirable. A titanium oxide content is 5 - 15 % of the weight preferably three to 20% of the weight in general to polyethylene.

[0048] polyethylene covering paper can also use the object in which a mat side which performs the so-called mold attachment processing and is acquired with the usual photographic printing paper, and the silky surface were formed, by this invention, in case melting push appearance also of also using as glossy paper is carried out and it coats polyethylene on a stencil paper front face.

[0049] After preparing an ink absorbing layer and a back layer, the amount of the polyethylene used of the front flesh side of stencil paper is damp and range whose 20-40-micrometer and back layer side the polyethylene layer by the side of an ink absorbing layer is 10-30 micrometers in general, although it is chosen so that the curl by highly-humid-izing may be optimized.

[0050] Furthermore, as for the above-mentioned polyethylene covering paper base material, it is desirable to have the following properties.

[0051] ** It is desirable that a lengthwise direction is [2 thru/or 30kg, and a longitudinal direction] 1 thru/or 20kg by the reinforcement specified by :JIS-P-8113 in hauling strength.

[0052] ** Tear reinforcement : 10 thru/or 300g, and a longitudinal direction have [a lengthwise direction] 20 thru/or desirable 400g by the convention approach by JIS-P-8116.

[0053] ** Clerks stiffness : 20-400g/100 are desirable.

[0054] ** Compressibility ≥ 103 kgf/cm² ** surface smoothness : 500 seconds or more, although the Beck smoothness specified to JIS-P-8119 has 1000 desirable seconds or more especially as a glossy surface, it may be less than [this] in the so-called mold attachment article.

[0055] ** surface roughness: — the wave filtration waviness curve drawn on with a cut-off value [of 0.8mm] conditions from the cross-section curve measured by the approach specified to JIS-B-0610 — a criteria tone — as 2.5mm — wave filtration max — the time of measuring a wave — 100 point of measurement of the arbitration — max — it is desirable that a wave is [a point 6 micrometers or more] less than five pieces and that the ten-point average of roughness height is less than 4 micrometers.

[0056] ** Surface glossiness : when it measures at the include angle of 60 degrees by the approach specified to JISZ-8741, it is 90% or more especially preferably 70% or more preferably 30% or more.

[0057] ** Surface whiteness degree : when it measures by the approach indicated by JIS-Z-8722 and displays according to JIS-Z-8729, [0058]

[External Character 1]

L*は85%以上、特に90%以上が好ましい。

また、(a*, b*)は(-2, 2)、(4, 2)、(4, -8)

および(-3, -8)で囲まれる範囲の色調が好ましい。

[0059] ** Opacity : when it measures by the approach specified to JIS-P-8138, it is especially most preferably [94% or more of] desirable 90% or more 50% or more.

[0060] 15-50 micrometers of thickness of the polyolefine layer which covers a paper base material are 20-40 micrometers preferably. In consideration of the balance of the curl after painting ink absorptivity being optimized, according to the view usually performed with the printing paper base material for photographs, the polyolefine layer of the front flesh side of paper is optimized suitably, and is decided.

[0061] 100-300 micrometers of thickness of said base material are 130-250 micrometers preferably.

[0062] It is desirable to perform corona discharge treatment, undercoating processing, etc. to a base material in advance of spreading of an ink absorbing layer for the purpose, such as to enlarge bond strength of the various above-mentioned base materials and an ink television layer.

[0063] In this invention, the secondary particle which has a hydrophilic binder and the mean particle diameter of

30–200nm on a base material is contained in an ink absorptivity layer.

[0064] When the primary particle a hydrophilic binder and whose mean particle diameter are 30–200nm is used on a base material, an opening is not formed in the interior of this particle at all, but in order to secure the amount of openings to need, desiccation thickness increases remarkably, and the coat brittleness mentioned later becomes easy to get worse.

[0065] Moreover, when the secondary particle which has the mean particle diameter exceeding 200nm is used, the glossiness of an opening layer falls and a clear image is no longer obtained.

[0066] It falls or, as for on the other hand using the secondary particle which has the mean particle diameter of less than 30nm, formation of secondary floc with the stable handling nature and stability of the primary particle itself tends to change difficult.

[0067] Although a secondary particle makes the primary particle of the particle size of $1/5 - 1/20$ usually condense and is formed from a secondary particle, it is desirable to make a 3–15nm primary particle condense as a primary particle in this invention here.

[0068] Forming the floc of a secondary particle may make a primary particle condense the 2nd order in which phase that manufactures a record form. Moreover, for example The distributed object of the secondary particle condensed beforehand may be mixed with a hydrophilic binder, and you may apply on a base material. Moreover, a secondary particle may be formed, in case the dispersion liquid of a primary particle are mixed with a hydrophilic binder water solution and coating liquid is prepared. The hydrophilic binder currently distributed in the state of the primary [further] particle may be applied on a base material, and a secondary particle may be formed by heat treatment after a desiccation process or desiccation etc.

[0069] In this invention, the mean particle diameter of a secondary particle says the mean particle diameter of the secondary particle in the opening layer formed on the base material. The mean particle diameter of such a secondary particle observes the cross section and front face of an opening layer with an electron microscope, and is called for as the arithmetic average value (individual number average) in quest of the particle size of the secondary particle of 100 arbitration.

[0070] Here, the particle size of the secondary particle according to individual observes the particle with an electron microscope, measures the area of the projection image, and is called for as a diameter when assuming a circle equal to the area.

[0071] As a particle formed by the secondary condensation which can be used for this invention, although non-subtlety particles, such as a barium sulfate, a calcium carbonate, a zinc oxide, synthetic hectorite, and a silica, etc. are mentioned, especially a silica is desirable.

[0072] When the particle itself tends to condense a silica particle by the hydrogen bond by the surface silanol group and it is made to condense under existence of a hydrophilic binder like especially this invention, comparatively loose condensation (flocculation) is formed and high voidage is attained.

[0073] A silica particle is divided roughly into dry process and a wet method according to a manufacturing method. As a dry-process particle silica, the approach by the gaseous-phase method hydrolysis in the elevated temperature of silicon halide and the approach of carrying out heating hydride generation of silica sand and the corks with an arc process with an electric furnace, and smothering this are learned. Moreover, after the acidolysis of silicate generates active silica as a wet method silica, carry out a polymerization moderately, and it is made to condense and precipitate, and is obtained.

[0074] In the record form of this invention, there is no crack at the time of the film formation nature of a coat, i.e., spreading desiccation of a coat, and a gaseous-phase method silica is the most desirable from the point that a sex with the film is good.

[0075] The alumina denaturation silica processed in part with the alumina in the front face is also contained in the above-mentioned silica.

[0076] moreover, the above — although mean particle diameter can also use together wet method silicas, calcium carbonates, etc., such as colloidal silica which is 3–200nm, in addition to the gaseous-phase method silica used preferably, it is good for especially a gaseous-phase method silica to contain [of all particles] 30 % of the weight or more preferably 20% of the weight or more.

[0077] Although it is desirable in this invention that it is a primary particle with a mean particle diameter of 15nm or less, a primary particle 10nm or less is especially the most desirable from the height of glossiness and voidage.

[0078] There are various approaches in forming the secondary particle which is made to condense the above-mentioned primary particle and has the mean particle diameter of 30–200nm. For example, change the pH of the dispersion liquid of a uniform primary particle, or once forming the homogeneity coat of an approach and a primary particle which the hydrophilic binder water solution which can consider weak coupling, such as hydrogen bond, as the approach and the particle which add inorganic ion and cause condensation of a particle is added [coat], and makes condensation cause, apply a condensation accelerator, or make it sink in, or there are a method of causing condensation by heat treatment etc., the approach of combining these approaches, etc.

[0079] Moreover, like the above-mentioned, a mixing front with a hydrophilic binder, and after mixing, either after the time of spreading desiccation or desiccation can choose the optimal approach, and can carry out at the formation time of secondary floc.

[0080] In the record form of this invention, as a hydrophilic binder used combining the above-mentioned particle, although polyvinyl alcohol and its derivative, polyalkylene oxide, a polyvinyl pyrrolidone, gelatin, hydroxyl ethyl cellulose, cull BOKIRU methyl cellulose, a pullulan, casein, a dextran, etc. can be used, it is desirable from the point of the film strength immediately after printing that the bloating tendency and the solubility over the high-boiling point organic solvent and water which ink contains use a low hydrophilic binder.

[0081] In especially this invention, polyvinyl alcohol is desirable, and average degree of polymerization is [average degree of polymerization] 2000 or more polyvinyl alcohol most preferably 1000 or more especially. Moreover, especially whenever [saponification / of desirable polyvinyl alcohol / 80 – 100% of] is desirable 70 to 100%.

[0082] Although the particle for forming the opening layer of the record form of this invention and the ratio of a hydrophilic binder may change with the class of hydrophilic binder, the class of particle, the magnitude of the interaction of particle size, a hydrophilic binder, and a non-subtlety particle, etc., generally particles are 4–10 in a weight ratio to a hydrophilic binder.

[0083] When the maximum delivery of the ink in which a ratio exceeds 30 capacity % to the high-boiling point organic solvent in ink especially, and ink exceeds 25ml per two 1m of record forms, as for the ratio of the non-subtlety particle to a hydrophilic binder, 5–10 are desirable at a weight ratio.

[0084] It is desirable to add the hardening agent which can construct a bridge with said hydrophilic binder into the opening layer of the above-mentioned record form at the point of improving the film strength after printing which is amelioration of the film formation nature of an opening layer, the water resisting property of a coat, and the purpose of this invention. Inorganic hardening agents, such as an organic hardening agent which contains an epoxy group, an ethylene imino group, an activity vinyl group, etc. as such a hardening agent, chromium alum, a way acid, or way sand, are mentioned.

[0085] Especially when a hydrophilic binder is polyvinyl alcohol, the epoxy system hardening agent which has at least two epoxy groups in a molecule, a way acid, or way sand is desirable. 1–200mg per above-mentioned binder [hydrophilic] 1g of additions of a hardening agent is 2–100mg preferably.

[0086] Various kinds of additives can be made to contain if needed in the layer of the arbitration by the side of the ink receptiveness layer of the ink jet record form of this invention.

[0087] For example, an ultraviolet ray absorbent given in JP,57–74193,A, a 57–87988 official report, and a 62–261476 official report, JP,57–74192,A, a 57–87989 official report, a 60–72785 official report, The fading inhibitor indicated by a 61–146591 official report, JP,1–95091,A, the 3–13376 official report, etc., An anion, a cation or the various surfactants of Nonion, JP,59–42993,A, The fluorescent brightener indicated by a 59–52689 official report, a 62–280069 official report, a 61–242871 official report, JP,4–219266,A, etc., Various well-known additives, such as lubricant, such as pH regulators, such as a sulfuric acid, a phosphoric acid, a citric acid, a sodium hydroxide, a potassium hydroxide, and potassium carbonate, a defoaming agent, and a diethylene glycol, antiseptics, a thickener, an antistatic agent, and a mat agent, can also be made to contain.

[0088] Into the configuration layer of the arbitration by the side of the ink absorptivity of the record form of this invention, an alkali-metal weak acid salt the poly allylamine of publications, such as the poly cation polyelectrolyte of JP,56–84992,A, a basic latex polymer of JP,57–36692,A, JP,4–15744,B, JP,61–58788,A, and a 62–174184 official report, and given in JP,61–47290,A etc. can be used more than a kind as a deck-watertight-luminaire-ized agent of an image.

[0089] The amount of the spreading solid content by the side of the ink recording surface in the ink jet record form of this invention has in general desirable 5 – 40 g/m², and its 10 – 30 g/m² is more desirable. In addition, from the field of prevention of the curl after record image formation, it is good to form as thinly as possible.

[0090] Moreover, 40 – 80% of the voidage of the ink absorption layer of a record form is desirable. When voidage is less than 40%, in order to secure required void volume, the thickness of an ink absorptivity layer increases too much, and the crack of an ink absorptivity layer and an adhesive property with a base material tend to become a problem. On the other hand, when voidage exceeds 80%, there is an inclination to become easy for the reinforcement of the coat after printing which is the effectiveness of this invention to fall. It is the range whose voidage is 50 – 70% preferably.

[0091] Moreover, although the desiccation thickness of an opening layer is mainly determined by said voidage and void volume, its 25–55 micrometers are especially more desirable than the viewpoint of crack prevention of a coat 20–60 micrometers.

[0092] Voidage is expressed with the following formulas from the desiccation thickness of void volume and an opening layer here.

[0093] Voidage (%) = $100 \times (\text{void volume (ml/m}^2\text{)} / \text{desiccation thickness (micrometer)})$

However, when void volume measures the ink absorptivity layer side of a record form by the approach indicated

by the liquid absorptivity test method (Bristow law) of J.TAPPI paper pulp test-method No.51 -87 paper and the paper board by this invention, absorption time amount is expressed with the amount of liquid transition in 2 seconds (ml/m²). In addition, although the liquid used at this time is pure water (ion exchange water), in order to make distinction of measurement area easy, less than 2% of water soluble dye may be contained.

[0094] In order to adhere at the time of piling up immediately after curl prevention or printing to the opposite side and to raise prevention and ink-proof imprint nature further, as for the ink absorptivity layer side of the record form of this invention, it is desirable to prepare the back layer of various classes.

[0095] Although the configuration of a back layer changes also with the class of base material, thickness, and the configuration and thickness of an ink absorptivity layer, generally a hydrophilic binder and a hydrophobic binder are used. The range of the thickness of a back layer is usually 0.1-10 micrometers.

[0096] Moreover, it adheres to a back layer as other record forms, and-izing of the front face can be carried out [split face] to prevention, note nature amelioration, and a pan for conveyance nature amelioration within an ink jet recording device. A well-known particle organic [an organic particle size is 2-20 micrometers], or inorganic is preferably used for this purpose.

[0097] In the ink jet record approach of this invention, the thing of the amount [in / in said void volume which a record form has / the maximum ink discharge quantity] of high-boiling point organic solvents which it has 3 or more times is required.

[0098] Here, the maximum ink discharge quantity is an amount from which the amount of ink breathed out by per two 1m of record forms becomes max in the conditions which say the amount of maximum regurgitation ink at the time of recording the usual full color image, and record the usual image. When the case where, as for this, the maximum concentration of the ink of a specific color is formed according to the ink regurgitation conditions of a recording device becomes the maximum ink discharge quantity, Although there may be various cases when the case where black is formed by further 3 colors when the case where the color formed by some two specific colors is formed becomes a maximum delivery becomes a maximum delivery It has set to this invention, and even if it is the case of a gap, it is necessary to make it 3 or more times of the amount of openings to the amount of high-boiling point organic solvents in the amount of the maximum ink.

[0099] When the reinforcement of the coat after printing becomes inadequate to the amount of high-boiling point organic solvents in the amount of the maximum ink when the amount of openings is less than 3 times, or paper is piled up, and saved especially by the high-humidity condition, it becomes easy to imprint a color.

[0100] Next, the water-soluble ink used for the ink jet record approach of this invention is explained below.

[0101] The water-soluble ink used for this invention is usually water soluble dye and a solvent object, and a record liquid that consists of other additives. Although water soluble dye, such as direct dye well-known as water soluble dye at an ink jet, acid dye, basic dye, reactive dye, or a food dye, can be used, direct dye or acid dye is desirable.

[0102] Although it becomes as a subject, when liquid ink dries water, in order that a color may deposit and the solvent of water color ink may prevent the blinding in a nozzle tip or an ink supply path, a high-boiling point organic solvent with the boiling point liquefied above about 120 degrees C is usually used at a room temperature. A high-boiling point organic solvent needs to have a high miscibility to water, while it is required that it should have vapor pressure far lower than water, since it has the operation which formed elements, such as a color, deposit and prevents generating of a big and rough sludge when water evaporates.

[0103] such a purpose — as a high-boiling point organic solvent — the organic solvent of a high-boiling point — usually — many — use — now, ** as an example Ethylene glycol, propylene glycol, a diethylene glycol, Triethylene glycol, a glycerol, the JICHIREN glycol monomethyl ether, The diethylene-glycol monobutyl ether, the triethylene glycol monobutyl ether, The glycerol monomethyl ether, 1 and 2, 3-butane triol, 1 and 2, 4-butane triol, Alcohols, such as 1, 2, 4-pentanetriol, 1 and 2, 6-hexane triol, thiodiglycol, triethanolamine, and a polyethylene glycol (average molecular weight is about 300 or less), are mentioned. Moreover, dimethylformamide, N-methyl pyrrolidone, etc. can be used also besides having described above.

[0104] Also in the high-boiling point organic solvent of these many, the low-grade alkyl ether of the polyhydric alcohol of polyhydric alcohol, such as a diethylene glycol, triethanolamine, and a glycerol, and the triethylene glycol monobutyl ether etc. is desirable.

[0105] As an additive of others which water color ink contains, a pH regulator, a sequestering agent, an antifungal agent, a viscosity controlling agent, a surface tension regulator, a wetting agent, a surfactant, a rusr-proofer, etc. are mentioned, for example.

[0106] In order that the wettability to a record form may make water-color-ink liquid good, it is the purpose which stabilizes the regurgitation from an ink jet nozzle, and in 25 degrees C, it is desirable to have the surface tension of 28 - 40 dyne/cm within the limits preferably 25 to 50 dyne/cm.

[0107] Moreover, the viscosity of water color ink is usually 2.5 - 5cp preferably two to 8 cp in 25 degrees C.

[0108] The range of pH of water color ink is usually 4-10.

[0109] In the ink jet record approach of this invention, since the diameter of the minimum dot with a diameter of

about 20–60 micrometers is obtained in the record paper as a minimum liquid ink drop in the case of the capacity of 1–30x10⁻³nl, it is desirable. The color-print printed with such a diameter of a dot gives a high-definition image. It is the case where the drop which has the volume of 2–20x10⁻³nl preferably is breathed out as the minimum drop.

[0110] Moreover, in the method recorded about a Magenta and cyanogen at least in the ink whose concentration is two kinds from which said water-soluble ink differs more than twice respectively, since low-concentration ink is used, it is hard coming to carry out discernment of a dot in the highlights section, but this invention can be applied, also when this recording method is adopted.

[0111] In the ink jet record approach of this invention, as the record approach, various kinds of well-known methods can be used conventionally, and the detail is indicated by the trend (the volume for Koichi Nakamura, March 31, Heisei 7, the Japan science-information incorporated company issue) of for example, an ink jet record technique.

[0112] In the ink jet record approach of this invention, combining suitably approaches, such as making [many / as possible] thickness for the void volume of the record form which lessens the amount of maximum regurgitation ink as much as possible which lowers the ratio in the ink of a high-boiling point organic solvent, the approach of making void volume to the amount of high-boiling point organic solvents in the amount of the maximum ink 3 or more times sets up the optimal conditions, and is chosen.

[0113] In this invention, if the amount of organic solvents which remains in the opening layer after printing exceeds one third of void volume, as described above, the film strength immediately after printing will tend to fall, and will become. Ink with the high content of a high-boiling point organic solvent (for example, ink containing the high-boiling point organic solvent more than 40 capacity %) is used. Although the amount of residual organic solvents needs to create to a sake more [far] void volume than the void volume needed for absorbing ink completely in the case of printing also in the location which carried out the maximum ink regurgitation making it be 1/3 or less [of the amount of openings] In this case, it will be necessary to thicken thickness of an ink absorption layer superfluously, and becomes easy to produce a crack etc. In this invention from this viewpoint, 30% or less is desirable 35% or less by capacity especially as an amount of ink solvents.

[0114] On the other hand, although the minimum of the content of a high-boiling point organic solvent is decided from mainly giving blinding, the optimal viscosity, and surface tension to ink etc., it is desirable to contain more than 15 capacity % preferably more than 10 capacity % mainly from a viewpoint of blinding prevention.

[0115] the solvent whose amount when the high-boiling point organic solvent ratio in ink being expressed with capacity % of the high-boiling point organic solvent which ink contains here, for example, measuring by the high-boiling point organic solvent independent is 10ml — ink 100ml — when contained in inside, it should display as 10% Moreover, when a high-boiling point organic solvent is two or more kinds, the ratio of each high-boiling point organic solvent is added and expressed.

[0116] The most effective approach of lessening the amount of maximum regurgitation ink as much as possible is making the diameter of a dot as small as possible. In order to lose the white omission of the maximum concentration region, the number of dots per unit area increases, as the diameter of a dot becomes small, but the capacity per dot decreases conversely, and since there is more this reduction than the increment in the number of dots, the amount of ink to a record form usually decreases. Consequently, the thickness needed as void volume is also mitigated.

[0117] Therefore, since the amount of ink printed by the record form decreases with reduction of the diameter of a dot, it is desirable that the diameter at the maximum equator (diameter when assuming a circle equal to this in quest of the dot area when a single dot is printed in monochrome ink) of the dot used in this invention in a maximum-density region sets 80 micrometers or less especially to 60 micrometers.

[0118] Furthermore, that it is easy to cause a crack by the impact from the outside etc. with under the handling at the time of, as for thickness becoming carelessly and thick although the effectiveness of this invention is easy to be acquired the more the more there is much void volume, the brittleness of a coat deteriorating, and being a desiccation process at the time of manufacture, or it being damp, and saving, other papers, a writing implement, etc., it becomes, or an adhesive property with a base material tends [further] to fall, and it becomes. Especially, as for the crack at the time of manufacture, it is desirable to make desiccation thickness of a coat as thin as possible in many cases with the fall of gloss, since the effect on image quality is also comparatively large.

[0119] As mentioned above, as mentioned above, 40 to 80%, the voidage of a coat is 50 – 70% preferably, and it is most desirable to make it void volume become the 3 to 4 times as much range as the amount of high-boiling point organic solvents at the time of the maximum ink regurgitation. Especially use of the hardening agent which constructs a bridge in the hydrophilic binder of a coat for this purpose is desirable.

*** NOTICES ***

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2. **** shows the word which can not be translated.
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EXAMPLE

[Example] Although the example of this invention is given and explained below, this invention is not limited to these examples.

[0121] It was obtained by the gaseous-phase method example 1 mean particle diameter is about 7nm, and 150g of primary particle silica powder was added in 1000ml of pure water, the high-speed homogenizer distributed, and pale clear dispersion liquid were obtained. Next, in this silica water dispersion (I), average degree of polymerization added gradually 2% polyvinyl alcohol water-solution (II) (ethyl acetate is contained for surface active agent -1 8% of the weight 0.1% of the weight) 1250ml whenever [saponification / whose] is 88% by 3500. Subsequently, 20ml of 4% way sand water solutions was added as a hardening agent, the high-speed homogenizer distributed, and white translucent-like coating liquid was obtained (this liquid is 6 times in a weight ratio to polyvinyl alcohol about a silica).

[0122] Next, the paper base material which covered both sides of the stencil paper of 170 g/m² with polyethylene (an anatase mold titanium dioxide is contained 13% of the weight in the polyethylene layer by the side of 240 micrometers in thickness, and a recording surface.) the back layer which makes solid content Tg=65 degree C acrylic latex resin at a rear-face side, and is contained two times 0.3 g/m by making into a mat agent the silica 0.6 g/m² and whose mean diameter are about 13 micrometers — having — it prepared.

[0123] For 95.2% and surface glossiness (75-degree specular gloss), the opacity of the above-mentioned polyethylene covering paper is 2.5mm of criteria length about the wave filtration waviness curve drawn on with a cut-off value [of 0.8mm] acquired from the cross-section curve when measuring the field by the side of an ink absorption layer 90.3% according to JIS-B -0610 conditions. wave filtration max — 100 point of measurement of the arbitration when measuring a wave — max — the number of points 6 micrometers or more was [the wave] one, and the ten-point average of roughness height of the Beck smoothness of the field by the side of 1.3 micrometers and an ink absorption layer was 2100 seconds.

[0124] The 40-degree C coating liquid obtained as mentioned above was applied to the recording surface side of the above-mentioned polyethylene covering paper, and was made to once cool so that spreading coat temperature may turn to 15 degrees C or less (for 20 seconds). Subsequently, the 25-degree C wind was sprayed for the 20-degree C wind for 30 seconds, for 60 seconds and a 45 more-degree C wind were sprayed for 30 seconds and for a 35-degree C wind one by one for 120 seconds, it dried, 25 more degrees C and the ambient atmosphere of 50% of relative humidity were passed for 30 seconds, gas conditioning was carried out, and the record form -1 was produced.

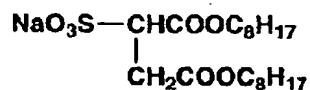
[0125] Next, in the record form -1, the silica was changed into the thing and the 20nm thing whose primary particle size is 13nm, and the record form -2 and the record form -3 as well as the record form -1 were produced.

[0126] The record form obtained as mentioned above was saved for five days at 38 degrees C and 40 - 60% of relative humidity.

[0127]

[Formula 1]

界面活性剤-1



[0128] The above-mentioned record form - About each of 1-3, the mean particle diameter of desiccation thickness and a secondary particle, void volume, and glossiness were measured, and the result shown in Table 1 was obtained.

[0129] In addition, the mean particle diameter of a secondary particle observed the front face of each record form with the electron microscope, asked for the particle size of each particle as a diameter when assuming a circle equal to the area in quest of the projected area about 100 particles of the arbitration of each record form, respectively, and asked for the mean particle diameter of the secondary particle of each record form as an

arithmetic average of the particle size of 100 particles.

[0130] Moreover, the Kumagaya Riki Kogyo K.K. make and a Bristow testing-machine II mold (pressure type) were used for void volume, and it calculated the amount of transition for [contact time] 2 seconds as void volume.

[0131] Glossiness measured the specular gloss 75 degrees with the deflection photometer (VGS-101DP) by Nippon Denshoku Industries Co., Ltd.

[0132] On the other hand, the ink of the following presentations was adjusted as an object for ink jet recording ink -1.

[0133] [Recording ink -1]

Yellow ink Y-1 (high-boiling point organic-solvent ratio: 19.7%)

C. I. direct yellow 86 2.1g Diethylene glycol 15.3ml Glycerol 4.4ml 100ml is made with pure water (ion exchange water).

[0134]

Magenta ink M-1 (high-boiling point organic-solvent ratio: 21.2%)

The following Magenta color -1 1.8g Diethylene glycol 13.1ml Glycerol 8.1ml 100ml is made with pure water (ion exchange water).

[0135]

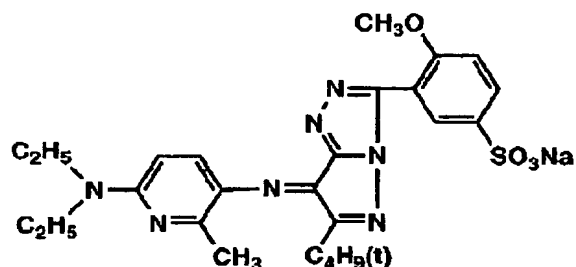
Cyanogen ink C-1 (high-boiling point organic-solvent ratio: 20.3%)

C. I. direct blue 199 2.8g Diethylene glycol 13.1ml Glycerol 7.2ml 100ml is made with pure water (ion exchange water).

[0136]

[Formula 2]

マゼンタ染料-1



[0137] the above-mentioned liquid ink was used and ink jet record of the regurgitation consistency was carried out by 720dpi (regurgitation spacing = about 35 micrometers) record form-1-3 by the on-demand mold ink jet recording head (diameter = of nozzle 25 micrometer, and each ink — drop diameter = — about [about 27 micrometers and / drop volume =] — regurgitation conditions were adjusted, respectively so that it might be set to 10x10-6 microl.) which makes ink breathe out with a piezo trembler. The amounts of maximum regurgitation ink at this time were about 8.1 ml/m² per ink 1 color. The amount when carrying out the maximum regurgitation of yellow, a Magenta, and the cyanogen ink to coincidence is 24.3 ml/m².

[0138] The above-mentioned record form - The following approaches estimated the film strength after drying and printing using 1-3, and ink jet recording ink.

[0139] (1) After saving [in coincidence] each color of yellow, a Magenta, and cyanogen for 30 minutes after printing on the highest regurgitation conditions with the drying above-mentioned ink jet printer at 23 degrees C and 65% of relative humidity, the paper of fine quality of 80 g/m² was saved in piles 200 sheets one whole day and night, and ink imprint nature was investigated on the following criteria.

[0140]

O : — completely — imprint-less O: — although the marks of an imprint of a color remain slightly, the image itself is hardly changeful — **:imprint trace is large, the adhesion of x:paper and an ink absorptivity layer from which a front face will be in a devitrification condition is large, and an image cannot remove paper finely, either — after printing, after saving on the same conditions for 24 hours, the same evaluation was also doubled in piles and paper was performed again.

[0141] (2) After leaving it for after [solid printing] two days of 3 color coincidence on the same conditions as drying evaluation of the film strength after printing (1), the continuation load (0-100g) be applied to the sapphire needle whose tip be 0.3mm in 23 degrees C and the environment of 80% of relative humidity using the **** strength test machine (Hayden try BOGIA, new east science incorporated company make), the film strength be examined, and it asked for the reinforcement by which a coat be destroy as a film strength.

[0142] If it is 30g or more in general by this evaluation approach, it can be said that it has the practically sufficiently high film strength.

[0143] The above-mentioned result is shown in Table 1.

[0144]

[Table 1]

記録用紙	2次粒子粒径	乾燥膜厚 (μm)	空隙容量 (ml/m^2)	空隙率 (%)	V/H	光沢度	乾 燥 性		印字後 皮膜強度
							30分後	24時間後	
1 (本発明)	60 μm	40	25.2	63	5.0	69%	◎	◎	90 g
2 (本発明)	140 μm	41	24.7	60	4.9	52%	◎	◎	>100 g
3 (比較例)	230 μm	42	25.4	60	5.1	14%	◎	◎	>100 g

V/H : 最大インク吐出時高沸点有機溶媒量 (5.0ml) に対する空隙容量比率 (%)

[0145] Secondary floc is a record form although glossiness is falling greatly exceeding [when the record form -3 is used from the result shown in Table 1] 200nm. - Each of 1 and 2 has high glossiness. It turns out especially that it has high glossiness in the record form -1 whose particle size of a secondary particle is 100nm or less.

[0146] On the other hand, it is a record form. - In 1-3, in ink jet record of this example, each has the 4.9 to 5.1 times as many opening as this to V/H of high-boiling point organic solvents, i.e., the amount at the time of the maximum ink regurgitation, and it has drying [good].

[0147] As mentioned above, record form - If the record approach of this invention using 1 and 2 is followed, it turns out that it is compatible in the high film strength after high glossiness, drying [good], and printing.

[0148] The ink jet recording ink -1 used in the example 2 example 1 is changed into the following recording ink - 2, the amount of drops breathed out from a head is adjusted so that it may become the same amount as an example 1, and it is a record form. - The result which evaluates the film strength after drying and printing like an example 1 using 1-3, and is shown in Table 2 was obtained.

[0149] [Recording ink -2]

Yellow ink Y-2 (high-boiling point organic-solvent ratio: 26.3%)

C. I. direct yellow 86 2.1g Diethylene glycol 22.3ml Glycerol 4.0ml 100ml is made with pure water (ion exchange water).

[0150]

Magenta ink M-2 (high-boiling point organic-solvent ratio: 29.8%)

Magenta color -1 1.8g Diethylene glycol 22.0ml Glycerol 7.8ml 100ml is made with pure water (ion exchange water).

[0151]

Cyanogen ink C-2 (high-boiling point organic-solvent ratio: 29.7%)

C. I. direct blue 199 2.8g Diethylene glycol 24.6ml Glycerol 5.1ml 100ml is made with pure water (ion exchange water).

[0152]

[Table 2]

記録用紙	V/H	乾 燥 性		印字後 皮膜強度
		30分後	24時間後	
1 (本発明)	3.6	◎	◎	60 g
2 (本発明)	3.5	◎	◎	70 g
3 (比較例)	3.6	◎	◎	80 g

V/H : 最大インク吐出時高沸点有機溶媒量 (7.0ml) に対する空隙容量比率 (%)

[0153] It is a record form, even if it makes the amount of ink solvents increase and void volume falls to about 3.5 to 3.6 times of the high-boiling point organic solvent at the time of the maximum ink regurgitation from the result shown in Table 2. - If the record approach of this invention using 1 and 2 is followed, although the film strength

immediately after printing will fall a little rather than an example 1, it is in the level which should be satisfied enough practically.

[0154] The ink jet recording ink -1 used in the example of comparison -1 example 1 is changed into the following recording ink -3, the amount of drops breathed out from a head is adjusted so that it may become the same amount as an example 1, and it is a record form. - The result which evaluates the film strength after drying and printing like an example 1 using 1-3, and is shown in Table 3 was obtained.

[0155] [Recording ink -3]

Yellow ink Y-3 (high-boiling point organic-solvent ratio: 36.4%)

C. I. direct yellow 86 2.1g Diethylene glycol 31.8ml Glycerol 4.6ml 100ml is made with pure water (ion exchange water).

[0156]

Magenta ink M-3 (high-boiling point organic-solvent ratio: 37.8%)

Magenta color -1 1.8g Diethylene glycol 32.6ml Glycerol 5.2ml 100ml is made with pure water (ion exchange water).

[0157]

Cyanogen ink C-3 (high-boiling point organic-solvent ratio: 37.2%)

C. I. direct blue 199 2.8g Diethylene glycol 31.3ml Glycerol 5.9ml 100ml is made with pure water (ion exchange water).

[0158]

[Table 3]

記録用紙	V/H	乾燥性		印字後 皮膜強度
		30分後	24時間後	
1 (比較例)	2.8	×	△	20 g
2 (比較例)	2.7	×	△	25 g
3 (比較例)	2.8	△	△	30 g

V/H : 最大インク吐出時高沸点有機溶媒量 (9.0ml) に対する
空隙容量比率 (%)

[0159] This example of a comparison is a record form although it is the case where it is made 3 or less times to the high-boiling point organic solvent at the time of the maximum ink regurgitation. - Both 1-3 are known by that drying falls more greatly than examples 1 and 2, and is in the level from which the film strength after printing also gets worse in the high record form of especially glossiness, and may produce a problem practically.

[0160] Record form produced in the example 3 example 1 - Humid thickness is made to increase by about 20% in 1-3 using each coating liquid, respectively, and it is a record form. - It is a record form like 1-3. - 1A, 2A, and 3A were produced.

[0161] Secondary particle particle size, desiccation thickness, void volume, and glossiness were measured like the example 1.

[0162] Ink jet record was performed using the recording ink which, on the other hand, used the ink JIETO recording apparatus used in the example 1, and was used in the example 1 of a comparison as recording ink, and the film strength after drying and printing was investigated like the example 1. A result is shown in Table 4.

[0163]

[Table 4]

記録用紙	2次粒子粒径	乾燥膜厚 (μm)	空隙容量 (ml/m^2)	空隙率 (%)	V/H	光沢度	乾燥性		印字後 皮膜強度
							30分後	24時間後	
1 A (本発明)	60 μm	48	30.2	63	3.4	64%	◎	◎	50 g
2 A (本発明)	140 μm	48	30.5	63	3.4	50%	◎	◎	60 g
3 A (比較例)	230 μm	49	30.1	61	3.3	10%	◎	◎	60 g

V/H : 最大インク吐出時高沸点有機溶媒量 (9.0ml) に対する空隙容量比率 (%)

[0164] Although desiccation thickness and void volume increase in proportion [almost] to humid thickness by increasing the humid thickness at the time of spreading from Table 4, there is an inclination for glossiness to fall a little.

[0165] This will be because the crack of the letter of a crack slight on the front face of an ink absorptivity layer

has arisen at the time of spreading desiccation, if it sees in a detail.

[0166] Record form whose mean particle diameter of a secondary particle the film strength after drying [good] and printing is maintained when the amount of openings of a record form exceeds 3 times of the amount of high-boiling point organic solvents at the time of the maximum ink regurgitation, and is moreover 200nm or less even if it is the case where the ink which contains a high-boiling point organic solvent by high concentration from the result of Table 4 is used – When 1 and 2 are used, it turns out that high glossiness is also attained.

[0167] In the ink JIETO recording apparatus used in the example of comparison 2 example 1, regurgitation conditions were changed into the head adjusted, respectively so that the diameter of a drop by which diameter = of nozzle 30 micrometer and each ink are breathed out might be set to about 32 micrometers and drop volume = abbreviation 18x10⁻⁶ microl in an ink jet recording head (recording ink used what was used in the example 3). Moreover, record form which used the regurgitation consistency in the example 3 by 600dpi (regurgitation spacing **42 micrometer) – Ink jet record was carried out at 1A–3A. The amounts of maximum regurgitation ink at this time were about 10.2 ml/m² per ink 1 color. The amount when carrying out the maximum regurgitation of yellow, a Magenta, and the cyanogen ink to coincidence is 30.6 ml/m².

[0168] The film strength after drying and printing was evaluated like the example 1, and the result shown in Table 5 was obtained.

[0169]

[Table 5]

記録用紙	空隙容量	V/H	乾 燥 性		印字後 皮膜強度
			30分後	24時間後	
1 A (比較例)	30.2	2.7	×	△	15 g
2 A (比較例)	30.5	2.7	×	△	20 g
3 A (比較例)	30.1	2.7	△	○	25 g

V/H : 最大インク吐出時高沸点有機溶媒量 (11.3ml) に対する
空隙容量比率 (%)

[0170] Moreover, since the discharge quantity as [whole] a record form increased even if it made regurgitation spacing correspond to this and the amount of openings became 3 or less times according to increase of the diameter of a drop to the amount of high-boiling point organic solvents at the time of the maximum ink regurgitation even if it used the record form and recording ink which were used in the example 3 from the result of Table 5, the film strength after drying and printing fell.

[0171] Record form produced in the example 4 example 1 – Record form to which each humid thickness was made to increase by about 40% in 1–3 – It is a record form about 1B–3B. – It produced like 1–3.

[0172] Record form – The result of the particle size of the secondary particle of 1B, 2B, and 3B, void volume, and glossiness is shown in Table 6.

[0173] Furthermore, the ink jet recording device used in the example 2 of a comparison estimated it the example 2 of a comparison similarly using the recording ink used in the example 1 of a comparison, and the result shown in Table 6 was obtained.

[0174]

[Table 6]

記録用紙	2次粒子粒径	乾燥膜厚 (μm)	空隙容量 (ml/m ²)	空隙率 (%)	V/H	光沢度	乾 燥 性		印字後 皮膜強度
							30分後	24時間後	
1 B (本発明)	60 μm	55	35.4	64	3.1	56%	○	◎	40 g
2 B (本発明)	140 μm	56	35.8	64	3.2	42%	○	◎	50 g
3 B (比較例)	240 μm	56	35.6	64	3.2	9%	○	◎	60 g

V/H : 最大インク吐出時高沸点有機溶媒量 (11.3ml) に対する空隙容量比率 (%)

[0175] From the result of Table 6, although the amount of openings increases according to the further increase of spreading thickness, glossiness falls further. However, record form – If it is 1B and 2B extent, although it is in the level which can be permitted somehow practically, the gloss of 3B is extinguished completely and has become the so-called mat side.

[0176] Moreover, if the film strength after drying or printing is measured against examples 1 and 2, although it will fall from the result of Table 6, the good result is shown if compared with the examples 1 and 2 of a comparison.

[0177] Record form produced in the example 5 example 1 – Record form which does not add way sand as a hardening agent in 1–3 – 1C, 2C, and 3C were produced

[0178] It is a record form except having changed the polyvinyl alcohol concentration of a water solution (II) to 4% in the record form produced in the example 1. - Record form-1D, 2D, and 3D were produced like 1-3.

[0179] Record form produced in the example 1 - It is a record form except average degree of polymerization having changed polyvinyl alcohol into the polyvinyl alcohol whenever [saponification / whose] is 88% in about 1700 in 1-3. - It is a record form like 1-3. - 1E, 2E, and 3E were produced.

[0180] Moreover, record form produced in the example 1 - In 1-3, a 70-100-degree C wind is sprayed, and it dries, without cooling after applying in the polyethylene covering paper at the time of desiccation, and is a record form. - 1F, 2F, and 3F were produced.

[0181] Desiccation thickness, void volume, and glossiness were investigated for each above-mentioned record form like the example 1. A result is shown in Table 7.

[0182] On the other hand, the film strength after drying and printing was investigated like the example 2 using the recording ink used in the example 2. A result is shown in Table 7.

[0183]

[Table 7]

記録用紙	2次粒子粒径	乾燥膜厚 (μm)	空隙容量 (ml/m^2)	空隙率 (%)	V/H	光沢度	乾燥性		印字後 皮膜強度
							30分後	24時間後	
1 C (本発明)	60 μm	41	24.4	59	3.5	61%	◎	◎	50 g
2 C (本発明)	140 μm	42	24.0	57	3.4	49%	◎	◎	50 g
3 C (比較例)	230 μm	41	24.7	60	3.5	11%	◎	◎	60 g
1 D (比較例)	50 μm	37	17.9	48	2.6	73%	×	△	10 g
2 D (比較例)	130 μm	38	18.3	48	2.6	59%	×	△	10 g
3 D (比較例)	220 μm	37	18.4	50	2.6	36%	×	△	20 g
1 E (本発明)	60 μm	40	24.6	62	3.5	55%	◎	◎	60 g
2 E (本発明)	140 μm	41	25.7	63	3.7	43%	◎	◎	80 g
3 E (比較例)	230 μm	41	25.9	63	3.7	8%	◎	◎	>100 g
1 F (比較例)	60 μm	35	17.8	51	2.5	51%	×	△	10 g
2 F (比較例)	140 μm	36	18.3	51	2.6	40%	×	△	10 g
3 F (比較例)	230 μm	36	19.5	54	2.8	10%	×	○	30 g

V/H ; 最大インク吐出時高沸点有機溶媒量 (7.0ml) に対する空隙容量比率 (%)

[0184] It is a record form when way sand is removed as a hardening agent from the result of Table 7 (record form - 1C-3C). - Although the film strength after printing and glossiness are falling a little as compared with 1-3, void volume and drying hardly change.

[0185] Although glossiness improves when the amount of the polyvinyl alcohol used is doubled in the record form -1 and the ratio of the hydrophilic binder to a non-subtlety particle is lowered to one half, about 2/of void volume is set to 3, the void volume to the amount of high-boiling point organic solvents becomes 3 or less times, and the film strength after drying or printing is falling greatly.

[0186] In the record form -1, although glossiness is ***** (ing) when polyvinyl alcohol is changed into the lower thing of average degree of polymerization, when way sand is removed in general, it has drying [near] and a near film strength.

[0187] Drying and a film strength not only got worse, but by the sample which carried out stoving, without cooling after applying in the case of manufacture of the record form -1, and making it set, void volume fell and the glossy fall accompanying a crack was accepted.

[Translation done.]

(19) 日本国特許庁 (J P)

(12) 公開特許公報 (A)

(11) 特許出願公開番号

特開平10-175365

(43) 公開日 平成10年(1998) 6月30日

(51) Int.Cl.⁶

識別記号

F I

B 4 1 M 5/00

B 4 1 M 5/00

A

C 0 9 J 129/04

C 0 9 J 129/04

B

Z

審査請求 未請求 請求項の数 7 O L (全 15 頁)

(21) 出願番号

特願平8-339539

(22) 出願日

平成 8 年(1996)12月19日

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(54) 【発明の名称】 インクジェット記録方法

(57) 【要約】

【課題】 低吸水性支持体上に空隙構造からなるインク吸収性層を有するインクジェット記録用紙に、水性インクを用いてインクジェット記録する際に、高光沢性と印字後の皮膜の早い乾燥性や良好な物理的な特性を両立させたインクジェット記録方法を提供する。

【解決手段】 非吸水性支持体上にインク吸収性層を有する記録用紙に、少なくともイエロー、マゼンタおよびシアンの水溶性インクで記録するインクジェット記録方法において、該記録用紙が親水性バインダーと30～200nmの平均粒径を有する2次微粒子を含有する空隙層を有するインクジェット記録用紙であって、該空隙層の空隙容量が、インク吐出量が最大の時のインクが含有する高沸点有機溶媒の容積の3倍以上であることを特徴とするインクジェット記録方法。

【特許請求の範囲】

【請求項1】 非吸水性支持体上にインク吸収性層を有する記録用紙に、少なくともイエロー、マゼンタおよびシアンの水溶性インクを用いて記録を行うインクジェット記録方法において、該記録用紙が、親水性バインダーと30～200nmの平均粒径を有する2次微粒子を含有する空隙層を有するインクジェット記録用紙であって、該空隙層の空隙容量が、インク吐出量が最大の時のインクが含有する高沸点有機溶媒の容量の3倍以上であることを特徴とするインクジェット記録方法。

【請求項2】 前記2次微粒子がシリカであることを特徴とする請求項1記載のインクジェット記録方法。

【請求項3】 前記2次粒子の親水性バインダーに対する比率が重量比で4～10であることを特徴とする請求項1又は2記載のインクジェット記録方法。

【請求項4】 前記親水性バインダーがポリビニルアルコールであることを特徴とする請求項1、2又は3記載のインクジェット記録方法。

【請求項5】 前記空隙層が硬膜剤を含有することを特徴とする請求項1～4の何れか1項記載のインクジェット記録方法。

【請求項6】 前記水溶性インクが含有する高沸点有機溶媒の量がインクの容量に対して35容量%以下であることを特徴とする請求項1～5の何れか1項記載のインクジェット記録方法。

【請求項7】 前記非吸水性支持体が両面をポリオレフィンで被覆した紙支持体であることを特徴とする請求項1～6の何れか1項記載のインクジェット記録方法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、水性インクを用いて記録を行うカラーインクジェット記録方法に関し、特に高い光沢性とムラのない高画質で高級感のあるカラー画像を記録出来、かつ記録直後の取り扱い性を改善したインクジェット記録方法に関する。

【0002】

【従来の技術】インクジェット記録は、インクの微小液滴を種々の作動原理により飛翔させて紙などの記録シートに付着させ、画像・文字などの記録を行うものであるが、比較的高速、低騒音、多色化が容易である等の利点を有している。この方式で従来から問題となっていたノズルの目詰まりとメンテナンスについては、インクおよび装置の両面から改良が進み、現在では各種プリンター、ファクシミリ、コンピューター端末等、さまざまな分野に急速に普及している。

【0003】その詳細は例えば、インクジェット記録技術の動向（中村孝一編、平成7年3月31日、日本科学情報株式会社発行）に記載されている。

【0004】このインクジェット記録方式で使用される記録用紙としては、印字ドットの濃度が高く、色調が明

るく鮮やかであること、インクの吸収が早く印字ドットが重なった場合に於いてもインクが流れ出したり滲んだりしないこと、印字ドットの横方向への拡散が必要以上に大きくなく、かつ周辺が滑らかでぼやけないこと等が一般的には要求されている。

【0005】ところで、カラーインクジェット記録で得られる画質を写真に近づけようとする試みが近年数多く行われている。

【0006】これは大きくインク吸収性層に関する特性、記録用紙に形成されるドットに起因する画質の改良に関する特性、及び支持体に関する特性に大きく分けられる。

【0007】インク吸収性層を改良する試みとしては、インク吸収性層の透明性を高めて印字濃度を向上する、インク表面の平滑性を高めて光沢性を高める、あるいは最大インク吸収容量を十分確保して、最高濃度域でインクが溢れないようにすることであり、従来から広範な改良技術が提案されてきている。

【0008】一方、ドットに起因する画質向上の最大のポイントはドット1個1個が目視で識別できないようにすることであり、そのためにインク液滴を小液滴化すること、または特にハイライト部でのドットの識別が困難なようにするために染料濃度として低濃度のインクを併用すること等がポイントでありこの点を改良するために従来から種々の改良技術が提案されてきている。

【0009】また、記録用紙としてインクが比較的浸透しやすい普通紙、上質紙、あるいは通常のアート紙や吸水性の比較的大きなキャストコート紙等では基材中にインクが浸透するため、印字部でのみ記録後にしわが発生してプリント品質を大きく低下させる。また、インクが紙繊維中に浸透したり不透明性の高い白色顔料含有コート層中に浸透するために、最高濃度が出にくく鮮明な画像が得られにくい欠点がある。

【0010】更に、ドットの真円度が紙繊維や比較的大きなサイズの白色顔料が存在するために乱れ、これがインクジェット記録の際の画質の劣化の一因にもなっている。

【0011】以上の点から、インクジェット記録用紙として写真のような高級感のある画質を得るために、水性インクが浸透しにくい、例えば写真用支持体、特に両面をポリオレフィンで被覆した写真用の紙支持体上にインク吸収性層を塗布した記録用紙（たとえばIBM Technical Disclosure Bulletin (Vol. 21, NO. 6, 1978年、2502頁)、米国特許第3,889,270号、特開平7-179032号、同7-179025号、同7-32723号及び同8-174992号公報に記載されている）および白色プラスチックフィルム上にインク吸収性層を塗布した記録用紙（たとえば、特開昭61-135783号に記載されている）等が好ましく用いられるよ

うになってきている。

【0012】ところで、上記写真並の画質を達成するためには、低インク吸水性の支持体上に比較的透明性の高いインク吸収性層を設けることが特に好ましいことではあるが、インク吸収性層の表面がマット化して光沢低下したり、あるいはインク吸収層自体がかなり大きなマイクロ構造を有している場合などには、光沢の低下以外にインク吸収性層の不透明性が上がるなどして写真並の画質が達成しにくいことが多い。

【0013】支持体上に設けるインク吸収性層としては従来から数多くのものが知られているが、大きく2つのタイプに分類される。

【0014】その一つは膨潤型のインク吸収性層であり、親水性バインダーを主体とするインク吸収性層である。これはインク液滴を親水性バインダーの主として膨潤作用により一時的に保持し、印字後徐々にインクが含有する水分や高沸点有機溶媒を蒸発させていくものである。

【0015】このインク吸収性層を支持体上に設けた膨潤型記録用紙の利点はインク溶媒（水及び高沸点有機溶媒）が完全に蒸発した後では非常に高い光沢性と高い最高濃度が得られる点にある。一方で、この膨潤型記録用紙はインク吸収速度が後述する空隙型記録用紙に比べて遅く、高インク領域でビーディング等を起こして画質が低下しやすい問題があり、更にインク溶媒、特に高沸点有機溶媒の蒸発が極めて遅いために印字後しばらくは親水性バインダーが膨潤した湿潤状態に長期間置かれることに伴う問題がある。具体的には印字後数時間、場合により数日間印字表面を強く擦ったり紙などを重ねることができない状況にある。

【0016】上記膨潤型とは別の型のインク吸収性層として、インク吸収性層が空隙構造を有する空隙型記録用紙がある。この記録用紙はインクジェット記録の際にインクをこの空隙に一時的に保持することによりインクを吸収するものであり、インク吸収速度が膨潤型に比べて早く、高インク領域において画質の劣化が少ない。

【0017】また、この種のインク吸収性層は空隙容量がインク量に対して十分あれば、空隙構造中に有機溶媒が残存していたとしても、少なくとも表面は印字直後に見かけ上乾いた状態になり、表面に触れたりプリント同士を重ね合わせること等も一応可能となる。

【0018】この種のインク吸収性層としては、比較的透明性の高い層が形成される点から低屈折率（特に約1.6以下の屈折率が好ましい）でしかも粒径の小さな微粒子（特に200nm以下が好ましい）が好ましく用いられ、中でもかかる条件を満たすシリカ微粒子が特に好ましい。

【0019】そのような微粒子シリカをインクジェット記録用紙に使用する従来技術として、例えば特公平3-56552号には、1次粒径が10～30nmの気相法に

より得られた微粒子シリカを2次凝集させ、BET法による表面積が80～200m²/gの微粒子を形成させて含有するインク吸収層を有する記録用紙が記載されている。

【0020】また、前記特開平8-174992号にはポリオレフィン被覆紙支持体上に、平均粒径が10nm以下の無機微粒子と親水性バインダーを使用し、高い光沢度を得るインクジェット記録用紙が記載されている。

【0021】しかしながら、空隙構造を有するインク吸収性層の場合には表面の光沢性と印字後の表面の物理強度が相反する傾向が大きい。

【0022】すなわち、空隙層をミクロ的に見た場合、そこに含有される微粒子の大きさやミクロ的な空隙構造が200μmを越えると、印字後の表面の強度は良好で表面に触れたり紙などを重ね合わせてもインクが転写すると言った問題は生じにくい、光沢性が極端に低下する傾向が大きい。

【0023】また、微粒子の大きさやミクロ的な空隙構造を200nm以下にすると、光沢は徐々に向上してくるものの、印字後の表面の柔らかさが増大して試料を重ね合わせたりするとインク転写が部分的に起こり始めたり、インク吸収層側面に紙を重ねてその上から鉛筆などで書いた場合にその痕跡が残りやすくなる。特に空隙構造が100nm以下になるとこの問題がもっと大きくなる。

【0024】この印字直後の表面の柔らかさは前記の膨潤型インク吸収性層の表面状態に比べれば遥かに良好なものの、改良が望まれるレベルにある。

【0025】このような印字後の皮膜の強度に関する問題の原因としては水分と高沸点有機溶媒があるが、水分自体は空隙層中に残存している時間は比較的短時間のためにこうした問題はあまり大きな問題にはなりにくい、高沸点有機溶媒の蒸発は一般には室温で数日間という時間を要するために、この間の取り扱い性に制約を受けやすい。

【0026】この問題は印字後プリントを高湿状態で保存した場合に、皮膜に水分が余計多く維持されているために顕著に成る傾向がある。また、この問題はインク量の最大量が吐出された部分で最も起こりやすい。

【0027】空隙構造を200nm以下にした場合、なぜこの問題が生じやすくなるかの理由は定かではないが、一つにはインク吸収性層の表面の凹凸が小さくなり重ね合わせる紙などとの接触面積が大きくなること、および、空隙構造が微細化してくることにより外部から加えられた力で皮膜の構造がより破壊されやすくなったためではないかと推定される。

【0028】前記特開平8-174992号および特公平3-56552号には、かかる微粒子シリカを用いた記録用紙は比較的高いインク吸収性と光沢性を有しているが、前記した課題に対する解決策が与えられていな

い。

【0029】

【発明が解決しようとする課題】本発明は上記の実態に鑑みてなされたものであって、本発明が解決しようとする課題は、低吸水性支持体上に空隙構造からなるインク吸収性層を有するインクジェット記録用紙に、水性インクを用いてインクジェット記録する際に、高光沢性と印字後の皮膜の早い乾燥性や良好な物理的な特性を両立させたインクジェット記録方法を提供することにある。

【0030】

【課題を解決するための手段】上記本発明が解決しようとする課題は、非吸水性支持体上にインク吸収性層を有する記録用紙に、少なくともイエロー、マゼンタおよびシアンの水溶性インクで記録するインクジェット記録方法において、該記録用紙が親水性バインダーと30～200nmの平均粒径を有する2次微粒子を含有する空隙層を有するインクジェット記録用紙であって、該空隙層の空隙容量が、インク吐出量が最大の時のインクが含有する高沸点有機溶媒の容積の3倍以上であることを特徴とするインクジェット記録方法により達成される。

【0031】以下本発明を詳細に説明する。

【0032】本発明の記録用紙に用いられる非吸水性支持体としては、プラスチックフィルムや両面をポリオレフィンで被覆した紙支持体が好ましく用いられる。

【0033】プラスチックフィルム支持体としては、たとえばポリエチレン、ポリプロピレン、ポリスチレン、ポリエチレンテレフタレート、ポリエチレンナフタレート、トリアセチルセルロース、ポリ塩化ビニル、ポリイミド、ポリカーボネート、セロファンなどのプラスチックフィルム支持体等が好ましい。

【0034】これらのプラスチックフィルムは透明なもの、半透明なものおよび不透明なものを用途に応じて適宜使い分けることが出来る。

【0035】白色フィルムとする場合、少量の硫酸バリウム、酸化チタン、酸化亜鉛などの白色顔料をプラスチックフィルム支持体に含有させて得られた支持体をそのまま用いてもよく、また、透明なフィルム支持体の裏面側またはインク吸収性層側の支持体に近い側に白色顔料（酸化チタン、硫酸バリウムなど）を有する層を設けた支持体であっても良い。

【0036】また、両面をポリオレフィンで被覆した紙支持体としては従来カラー印画紙で通常用いられているポリエチレンで両面を被覆した紙支持体が好ましい。この場合、インク吸収性層側のポリエチレン樹脂層中にはアナターゼ型またはルチル型の酸化チタンをポリエチレンに対して3～20重量%含有させるのが、支持体の不透明度や白色度の向上、あるいは得られる画像の鮮鋭性の低下さえないことから好ましい。

【0037】本発明においては、高品位なカラー画像を得る観点より、白色フィルム支持体、あるいは両面をポ

リエチレンなどのポリオレフィンで被覆した紙支持体などが好ましく、特に低コストで高級感のあるポリオレフィンで両面を被覆した紙支持体が最も好ましい。

【0038】以下、特に好ましく用いられるポリエチレンで両面を被覆した紙支持体について説明する。

【0039】紙支持体に用いられる原紙は木材パルプを主原料とし、必要に応じて木材パルプに加えてポリプロピレンなどの合成パルプあるいはナイロンやポリエステルなどの合成繊維を用いて抄紙される。木材パルプとしてはLBKP、LBSP、NBKP、NBSP、LDP、NDP、LUKP、NUKPのいずれも用いることが出来るが短繊維分の多いLBKP、NBSP、LBSP、NDP、LDPをより多く用いることが好ましい。但し、LBSPおよびまたはLDPの比率は10重量%以上、70重量%以下が好ましい。

【0040】上記パルプは不純物の少ない化学パルプ（硫酸塩パルプや亜硫酸塩パルプ）が好ましく用いられ、又、漂白処理を行って白色度を向上させたパルプも有用である。

【0041】原紙中には、高級脂肪酸、アルキルケテンダイマー等のサイズ剤、炭酸カルシウム、タルク、酸化チタンなどの白色顔料、スターチ、ポリアクリルアミド、ポリビニルアルコール等の紙力増強剤、蛍光増白剤、ポリエチレングリコール類等の水分保持剤、分散剤、4級アンモニウム等の柔軟化剤などを適宜添加することが出来る。

【0042】抄紙に使用するパルプの濾水度はCSFの規定で200～500ccが好ましく、また、叩解後の繊維長がJIS-P-8207に規定される24メッシュ残分重量%と42メッシュ算分の重量%との和が30乃至70%が好ましい。なお、4メッシュ残分の重量%は20重量%以下であることが好ましい。

【0043】原紙の坪量は60乃至250gが好ましく、特に90乃至200gが好ましい。原紙の厚さは50乃至250μmが好ましい。

【0044】原紙は抄紙段階または抄紙後にカレンダー処理して高平滑性を与えることも出来る。原紙密度は0.7乃至1.2g/m²（JIS-P-8118）が一般的である。更に原紙剛度はJIS-P-8143に規定される条件で20乃至200gが好ましい。

【0045】原紙表面には表面サイズ剤を塗布しても良く、表面サイズ剤としては前記原紙中に添加できるサイズ剤と同様のサイズ剤を使用できる。

【0046】原紙のpHはJIS-P-8113で規定された熱水抽出法により測定された場合、5～9であることが好ましい原紙表面および裏面を被覆するポリエチレンは、主として低密度のポリエチレン（LDPE）および/または高密度のポリエチレン（HDPE）であるが他のLLDPEやポリプロピレン等も一部使用することが出来る。

【0047】特にインク受容層側のポリエチレン層は写真用印画紙で広く行われているようにルチルまたはアナターゼ型の酸化チタンをポリエチレン中に添加し、不透明度および白色度を改良したものが好ましい。酸化チタン含有量はポリエチレンに対して概ね3~20重量%、好ましくは5~15重量%である。

【0048】ポリエチレン被覆紙は光沢紙として用いることも、また、ポリエチレンを原紙表面上に熔融押し出してコーティングする際にいわゆる型付け処理を行って通常の写真印画紙で得られるようなマット面や絹目面を形成した物も本発明で使用できる。

【0049】原紙の表裏のポリエチレンの使用量はインク受容層やバック層を設けた後で低湿および高湿化でのカールを最適化するように選択されるが、概ねインク受容層側のポリエチレン層が20~40 μ m、バック層側が10~30 μ mの範囲である。

【0050】更に上記ポリエチレン被覆紙支持体は以下の特性を有していることが好ましい。

【0051】① 引っ張り強さ：JIS-P-8113で規定される強度で縦方向が2乃至30kg、横方向が1乃至20kgであることが好ましい。

【0052】② 引き裂き強度：JIS-P-8116による規定方法で縦方向が10乃至300g、横方向が20乃至400gが好ましい。

L*は85%以上、特に90%以上が好ましい。

また、(a*, b*)は(-2, 2)、(4, 2)、(4, -8)

および(-3, -8)で囲まれる範囲の色調が好ましい。

【0059】⑨ 不透明度：JIS-P-8138に規定された方法で測定したときに50%以上、特に90%以上、最も好ましくは94%以上が好ましい。

【0060】紙支持体を被覆するポリオレフィン層の膜厚は15~50 μ m、好ましくは20~40 μ mである。紙の表裏のポリオレフィン層はインク吸収性を塗設した後のカールのバランスを最適化されることを考慮して、通常写真用印画紙支持体で行われる考え方に従って適宜最適化して決められる。

【0061】前記支持体の厚みは100~300 μ m、好ましくは130~250 μ mである。

【0062】上記各種支持体とインク受像層の接着強度を大きくする等の目的で、インク受容層の塗布に先立って、支持体にコロナ放電処理や下引処理等を行うことが好ましい。

【0063】本発明においては、支持体上に親水性バインダーと30~200nmの平均粒径を有する2次微粒子をインク吸収性層中に含有する。

【0064】支持体上に親水性バインダーと平均粒径が30~200nmの1次粒子を用いた場合には、この粒子内部には全く空隙が形成されず、必要とする空隙量を確保するためには乾燥膜厚が著しく増大して、後述する

【0053】③ クラーク剛度：20~400g/100が好ましい。

【0054】④ 圧縮弾性率 $\geq 10^3$ kgf/cm²

⑤ 表面平滑度：JIS-P-8119に規定されるベック平滑度が500秒以上、特に1000秒以上が光沢面としては好ましいが、いわゆる型付け品ではこれ以下であっても良い。

【0055】⑥ 表面粗さ：JIS-B-0610に規定された方法で測定された断面曲線から、カットオフ値0.8mmの条件で導かれるろ波うねり曲線について、基準調2.5mmとしてろ波最大うねりを測定したときに、その任意の測定点100個で最大うねりが6 μ m以上の点が5個以内であること、また、10点平均粗さが4 μ m以内であるのが好ましい。

【0056】⑦ 表面光沢度：JIS-Z-8741に規定された方法で60度の角度で測定した時、30%以上、好ましくは70%以上、特に好ましくは90%以上。

【0057】⑧ 表面白色度：JIS-Z-8722に記載された方法で測定し、JIS-Z-8729に従って表示したとき、

【0058】

【外1】

皮膜脆弱性が悪化しやすくなる。

【0065】また、200nmを越える平均粒径を有する2次微粒子を用いた場合、空隙層の光沢度が低下し、鮮明な画像が得られなくなる。

【0066】一方、30nm未満の平均粒径を有する2次微粒子を用いることは1次粒子自体の取り扱い性や安定性が低下したり、あるいは安定な2次凝集体の形成が困難に成りやすい。

【0067】ここで2次微粒子は、2次微粒子より通常は1/5~1/20の粒径の1次粒子を凝集させて形成されるものであるが、本発明においては1次粒子として3~15nmの1次粒子を凝集させるのが好ましい。

【0068】また、2次微粒子の凝集体を形成するのは、記録用紙を製造するどの段階で1次粒子を2次凝集させてもよく、たとえば、あらかじめ凝集している2次微粒子の分散物を親水性バインダーと混合して支持体上に塗布してもよく、また、1次粒子の分散液を親水性バインダー水溶液と混合して塗布液を調液する際に2次粒子を形成してもよく、さらには1次粒子の状態で分散されている親水性バインダーを支持体上に塗布し、乾燥過程または乾燥後の熱処理などにより2次微粒子の形成をしても良い。

【0069】本発明においては、2次微粒子の平均粒径は支持体上に形成された空隙層における2次微粒子の平均粒径を言う。そのような2次微粒子の平均粒径は、空隙層の断面や表面を電子顕微鏡で観察し、100個の任意の2次微粒子の粒径を求めてその単純平均値（個数平均）として求められる。

【0070】ここで、個別の2次微粒子の粒径は、その粒子を電子顕微鏡で観察してその投影像の面積を測定し、その面積に等しい円を仮定した時の直径として求められる。

【0071】本発明に使用できる2次凝集で形成された微粒子としては、硫酸バリウム、炭酸カルシウム、酸化亜鉛、合成ヘクトライトおよびシリカ等の無機微粒子等が挙げられるが、特にシリカが好ましい。

【0072】シリカ微粒子は表面のシラノール基による水素結合により粒子自身が凝集しやすく、特に本発明の様に親水性バインダーの存在下で凝集を行わせた場合には比較的緩い凝集（軟凝集）が形成され高い空隙率が達成される。

【0073】シリカ微粒子は製造法により乾式法と湿式法に大別される。乾式法微粒子シリカとしてはハロゲン化珪素の高温での気相法加水分解による方法、およびケイ砂とコークスを電気炉でアーク法により加熱還元気化しこれを空気酸化する方法が知られている。また、湿式法シリカとしては珪酸塩の酸分解により活性シリカを生成した後、適度に重合させて凝集・沈殿させて得られる。

【0074】本発明の記録用紙においては皮膜の造膜性、すなわち皮膜の塗布乾燥時のひび割れがなく膜付き性が良好である点から気相法シリカが最も好ましい。

【0075】上記シリカにはその表面をアルミナで一部処理されたアルミナ変性シリカも含まれる。

【0076】又、上記好ましく用いられる気相法シリカ以外に、平均粒径が3~200nmのコロイダルシリカ等の湿式法シリカや炭酸カルシウム等を併用することもできるが、特に気相法シリカが全微粒子の20重量%以上、好ましくは30重量%以上を含有されるのが良い。

【0077】本発明においては15nm以下の平均粒径の1次微粒子であることが好ましいが、特に10nm以下の1次微粒子が光沢性と空隙率の高さから最も好ましい。

【0078】上記1次粒子を凝集させて30~200nmの平均粒径を有する2次微粒子を形成するには種々の方法がある。例えば、均一な1次粒子の分散液のpHを変えたり無機イオンを添加して粒子の凝集を起こす方法、微粒子と水素結合などの弱い結合をし得る親水性バインダー水溶液を添加して凝集を起こさせる方法、1次粒子の均一皮膜をいったん形成した後に凝集促進剤を塗布したり含浸させたり、熱処理などにより凝集を起こす方法、あるいはこれらの方法を組み合わせる方法等があ

る。

【0079】また、2次凝集粒子の形成時点は前述のごとく、親水性バインダーとの混合前や混合後、塗布乾燥時、あるいは乾燥後のいずれでも最適な方法を選択して行うことができる。

【0080】本発明の記録用紙において、上記微粒子と組み合わせて用いられる親水性バインダーとしては、ポリビニルアルコールおよびその誘導体、ポリアルキレンオキサイド、ポリビニルピロリドン、ゼラチン、ヒドロキシセルロース、カルボキシルセルロース、プルラン、カゼイン、デキストラン等を用いることができるが、インクが含有する高沸点有機溶媒や水に対する膨潤性や溶解性が低い親水性バインダーを使用するのが印字直後の皮膜強度の点から好ましい。

【0081】本発明では特にポリビニルアルコールが好ましく、中でも平均重合度が1000以上、最も好ましくは平均重合度が2000以上のポリビニルアルコールである。また、好ましいポリビニルアルコールのケン化度は70~100%、特に80~100%が好ましい。

【0082】本発明の記録用紙の空隙層を形成するための微粒子と親水性バインダーの比率は親水性バインダーの種類や微粒子の種類や粒径、親水性バインダーと無機微粒子との相互作用の大きさ等により変わり得るが、一般には親水性バインダーに対して微粒子が重量比で4~10である。

【0083】特にインク中の高沸点有機溶媒に比率が30容量%を越えるインクや、インクの最大吐出量が記録用紙1m²当たり25mlを越えるような場合には親水性バインダーに対する無機微粒子の比率は重量比で5~10が好ましい。

【0084】上記記録用紙の空隙層中には前記親水性バインダーと架橋し得る硬膜剤を添加するのが空隙層の造膜性の改良、皮膜の耐水性、および本発明の目的である印字後の皮膜強度を改善する点で好ましい。そのような硬膜剤としてはエポキシ基、エチレンイミノ基、活性ビニル基等を含有する有機硬膜剤、クロムみょうばん、ほう酸、あるいはほう砂等の無機硬膜剤が挙げられる。

【0085】親水性バインダーがポリビニルアルコールである場合には特に、分子中に少なくとも2個のエポキシ基を有するエポキシ系硬膜剤、ほう酸またはほう砂が好ましい。硬膜剤の添加量は上記親水性バインダー1g当たり1~200mg、好ましくは2~100mgである。

【0086】本発明のインクジェット記録用紙のインク受容性層側の任意の層中には、必要に応じて各種の添加剤を含有させることが出来る。

【0087】例えば、特開昭57-74193号公報、同57-87988号公報及び同62-261476号公報に記載の紫外線吸収剤、特開昭57-74192号、同57-87989号公報、同60-72785号

公報、同61-146591号公報、特開平1-95091号公報及び同3-13376号公報等に記載されている退色防止剤、アニオン、カチオンまたはノニオンの各種界面活性剤、特開昭59-42993号公報、同59-52689号公報、同62-280069号公報、同61-242871号公報および特開平4-219266号公報等に記載されている蛍光増白剤、硫酸、リン酸、クエン酸、水酸化ナトリウム、水酸化カリウム、炭酸カリウム等のpH調整剤、消泡剤、ジエチレングリコール等の潤滑剤、防腐剤、増粘剤、帯電防止剤、マツト剤等の公知の各種添加剤を含有させることもできる。

【0088】本発明の記録用紙のインク吸収性側の任意の構成層中には、画像の耐水化剤として特開昭56-84992号公報のポリカチオン高分子電解質、特開昭57-36692号公報の塩基性ラテックスポリマー、特公平4-15744号公報、特開昭61-58788号公報、同62-174184号公報等記載のポリアリルアミン、特開昭61-47290号公報記載のアルカリ金属弱酸塩等を一種以上用いることができる。

【0089】本発明のインクジェット記録用紙におけるインク記録面側の塗布固形分の量は概ね5~40g/m²が好ましく、10~30g/m²がより好ましい。なお、記録画像形成後のカールの防止という面からは、なるべく薄く形成するのが良い。

【0090】また、記録用紙のインク吸収層の空隙率は40~80%が好ましい。空隙率が40%未満の場合には必要な空隙容量を確保するためにインク吸収性層の膜厚が増大しすぎてインク吸収性層のひび割れや支持体との接着性が問題になりやすい。一方空隙率が80%を越えると、本発明の効果である印字後の皮膜の強度が低下しやすくなる傾向がある。好ましくは空隙率が50~70%の範囲である。

【0091】また、空隙層の乾燥膜厚は、前記空隙率と空隙容量により主に決定されるが、皮膜のひび割れ防止の観点より20~60μm、特に25~55μmが好ましい。

【0092】ここで空隙率は、空隙容量および空隙層の乾燥膜厚から以下の式で表される。

【0093】空隙率(%) = 100 × (空隙容量 (ml/m²) / 乾燥膜厚 (μm))

但し、空隙容量は本発明ではJ. TAPPI紙パルプ試験方法No. 51-87紙及び板紙の液体吸収性試験方法(ブリストー法)に記載された方法で記録用紙のインク吸収性層側を測定した時、吸収時間が2秒における液体転移量(ml/m²)で表される。なお、この時使用する液体は純水(イオン交換水)であるが、測定面積の判別を容易にするために2%未満の水溶性染料を含有していても良い。

【0094】本発明の記録用紙のインク吸収性層側とは反対側にはカール防止や印字直後に重ね合わせた際のく

つつき防止や耐インク転写性を更に向上させるために種々の種類のバック層を設けることが好ましい。

【0095】バック層の構成は支持体の種類や厚み、インク吸収性層の構成や厚みによっても変わるが一般には親水性バインダーや疎水性バインダーが用いられる。バック層の厚みは通常は0.1~10μmの範囲である。

【0096】また、バック層には他の記録用紙とのくつつき防止、筆記性改良、さらにはインクジェット記録装置内での搬送性改良のために表面を粗面化できる。この目的で好ましく用いられるのは粒径が2~20μmの有機または無機の公知の微粒子である。

【0097】本発明のインクジェット記録方法においては、記録用紙が有する前記空隙容量が、最大インク吐出量における高沸点有機溶媒量の3倍以上有することが必要である。

【0098】ここで、最大インク吐出量とは、通常のフルカラー画像を記録する際の最大吐出インク量を言い、通常の画像を記録する条件において、記録用紙1m²当たり吐出されるインク量が最大になる量である。これは、記録装置のインク吐出条件により、特定色のインクの最大濃度を形成する場合が最大インク吐出量になる場合、ある特定の2色で形成する色を形成する場合が最大吐出量になる場合、さらには3色で黒色を形成する場合が最大吐出量になる場合等種々のケースがあり得るが、本発明においてはいずれの場合であっても最大インク量における高沸点有機溶媒量に対して空隙量の3倍以上にする必要がある。

【0099】最大インク量における高沸点有機溶媒量に対して空隙量が3倍未満の場合には、印字後の皮膜の強度が不十分になったり、紙を重ねておいた場合、特に高温条件で保存した場合など染料が転写しやすくなる。

【0100】次に本発明のインクジェット記録方法に用いられる水溶性インクについて以下に説明する。

【0101】本発明に用いられる水溶性インクは、通常は水溶性染料及び液媒体、その他の添加剤から成る記録液体である。水溶性染料としてはインクジェットで公知の直接染料、酸性染料、塩基性染料、反応性染料あるいは食品用色素等の水溶性染料が使用できるが直接染料、または酸性染料が好ましい。

【0102】水性インクの溶媒は水を主体としてなるが、インク液が乾燥した際に染料が析出してノズル先端やインク供給経路での目詰まりを防止するために、通常沸点が約120℃以上で室温で液状の高沸点有機溶媒が使用される。高沸点有機溶媒は水が蒸発した際に染料などの固形成分が析出して粗大析出物の発生を防止する作用を持つために水よりはるかに低い蒸気圧を有することが要求される一方、水に対して混和性が高い必要がある。

【0103】そのような目的で高沸点有機溶媒としては高沸点の有機溶媒が通常多く使用されが、具体例とし

ては、エチレングリコール、プロピレングリコール、ジエチレングリコール、トリエチレングリコール、グリセリン、ジチレングリコールモノメチルエーテル、ジエチレングリコールモノブチルエーテル、トリエチレングリコールモノブチルエーテル、グリセリンモノメチルエーテル、1, 2, 3-ブタントリオール、1, 2, 4-ブタントリオール、1, 2, 4-ペンタントリオール、1, 2, 6-ヘキサントリオール、チオジグリコール、トリエタノールアミン、ポリエチレングリコール（平均分子量が約300以下）等のアルコール類が挙げられる。また、上記した以外にも、ジメチルホルムアミド、N-メチルピロリドン等も使用できる。

【0104】これらの多くの高沸点有機溶剤の中でも、ジエチレングリコール、トリエタノールアミンやグリセリン等の多価アルコール類、トリエチレングリコールモノブチルエーテルの多価アルコールの低級アルキルエーテル等は好ましいものである。

【0105】水性インクが含有するその他の添加剤としては、例えばpH調節剤、金属封鎖剤、防カビ剤、粘度調整剤、表面張力調整剤、湿潤剤、界面活性剤、及び防錆剤、等が挙げられる。

【0106】水性インク液は記録用紙に対する濡れ性が良好にするため及びインクジェットノズルからの吐出を安定化させる目的で、25℃において、25~50 dyne/cm、好ましくは28~40 dyne/cmの範囲内の表面張力を有するのが好ましい。

【0107】また、水性インクの粘度は通常25℃において2~8 cp、好ましくは2.5~5 cpである。

【0108】水性インクのpHは通常4~10の範囲である。

【0109】本発明のインクジェット記録方法において、最小インク液滴として $1\sim30\times10^{-3}$ n lの容量の場合、記録紙上で約20~60 μ mの直径の最小ドット径が得られるので好ましい。このようなドット径で印字されたカラープリントは高画質画像を与える。好ましくは $2\sim20\times10^{-3}$ n lの容積を有する液滴が最小液滴として吐出される場合である。

【0110】また、前記水溶性インクが、少なくともマゼンタおよびシアンについて、各々濃度が2倍以上異なる2種類のインクで記録する方式において、ハイライト部では低濃度のインクが使用されるためにドットの識別がしにくくなるが、本発明はかかる記録方式を採用した場合も適用できる。

【0111】本発明のインクジェット記録方法において、記録方法としては、従来公知の各種の方式を用いることができ、その詳細はたとえば、インクジェット記録技術の動向（中村孝一編、平成7年3月31日、日本科学情報株式会社発行）に記載されている。

【0112】本発明のインクジェット記録方法において、最大インク量における高沸点有機溶媒量に対する空

隙容量を3倍以上にする方法は高沸点有機溶媒のインク中の比率を下げる、最大吐出インク量を出るだけ少なくする、記録用紙の空隙容量を膜厚を出るだけ多くする等の方法を適宜組み合わせることで最適な条件を設定し選択される。

【0113】本発明においては、印字後の空隙層中に残存する有機溶媒量が空隙容量の1/3を越えると、前記したように印字直後の皮膜強度が低下しやすくなる。高沸点有機溶媒の含有量の高いインク（例えば40容量%以上の高沸点有機溶媒を含有するインク）を使用して、最大インク吐出した場所でも残存有機溶媒量が空隙量の1/3以下であるようにするためには、印字の際にインクを完全に吸収するのに必要とされる空隙容量より遥かに多い空隙容量を作成する必要があるが、この場合には不必要にインク吸収層の膜厚を厚くする必要が生じ、ひび割れなどが生じやすくなる。この観点から、本発明においてはインク溶媒量としては容量で35%以下、特に30%以下が好ましい。

【0114】一方、高沸点有機溶媒の含有量の下限は主に目詰まりや最適粘度や表面張力をインクに付与することなどから決められるが、主として目詰まり防止の観点から10容量%以上、好ましくは15容量%以上含有されるのが好ましい。

【0115】ここでインク中の高沸点有機溶媒比率は、インクが含有する高沸点有機溶媒の容量%で表され、例えば高沸点有機溶媒単独で測定した時の量が10 mlである溶媒をインク100 ml中に含有している場合に10%として表示したものとする。また、高沸点有機溶媒が2種類以上である場合、それぞれの高沸点有機溶媒の比率を加算して表す。

【0116】最大吐出インク量を出るだけ少なくする最も効果的な方法はドット径を可能な限り小さくすることである。ドット径が小さくなるに従って、最大濃度域の白抜けをなくするために単位面積当たりのドット数は増加するが、1ドット当たりの容量は逆に減少し、この減少の方がドット数の増加より多いために通常は記録用紙へのインク量は減少する。その結果、空隙容量として必要とされる膜厚も軽減される。

【0117】したがって、記録用紙に印字されるインク量はドット径の減少に伴って減少するので、本発明においては最高濃度域で使用されるドットの最大直径（単色インクで単ドットを印字した場合に、そのドット面積を求めこれと等しい円を仮定した時の直径）が80 μ m以下、特に60 μ mにするのが好ましい。

【0118】更に、空隙容量は多ければ多いほど本発明の効果は得られやすいが、膜厚が不用意に厚くなることは皮膜の脆弱性が劣化し、製造時の乾燥過程で、あるいは低湿で保存した際の取扱中や他の紙や筆記具などにより外部からの衝撃などにより、ひび割れを起こしやすくなりさらには支持体との接着性が低下しやすくな

る。特に、製造時のひび割れは光沢の低下を伴うことが多く、画質への影響も比較的大きいために皮膜の乾燥膜厚は可能な限り薄くするのが好ましい。

【0119】以上より、皮膜の空隙率は前述したように40～80%、好ましくは50～70%であり、最大インク吐出時の高沸点有機溶媒量の3～4倍の範囲に空隙容量がなるようにするのが最も好ましい。この目的のために、皮膜の親水性バインダーを架橋する硬膜剤の使用は特に好ましい。

【0120】

【実施例】以下に本発明の実施例を挙げて説明するが、本発明はこれらの例に限定されるものではない。

【0121】実施例1

平均粒径が約7nmの気相法により得られて1次微粒子シリカ粉末150gを純水1000ml中に添加し、高速ホモジナイザーで分散して青白い澄明な分散液を得た。次にこのシリカ水分散液(I)中に、平均重合度が3500でケン化度が88%の2%ポリビニルアルコール水溶液(II)(界面活性剤-1を0.1重量%、酢酸エチルを8重量%含有)1250mlを徐々に添加し、高速ホモジナイザーにて分散して白色半透明状の塗布液を得た(この液はシリカをポリビニルアルコールに対して重量比で6倍である)。

【0122】次に、170g/m²の原紙の両面をポリエチレンで被覆した紙支持体(厚さ240μm、記録面側のポリエチレン層中にアナターゼ型二酸化チタンを13重量%含有。裏面側にTg=65℃のアクリル系ラテックス樹脂を固形分として0.6g/m²および平均粒径が約13μmのシリカをマツト剤として0.3g/m²含有するバック層を有する)を用意した。

【0123】上記ポリエチレン被覆紙の不透明度は95.2%、表面光沢度(75度鏡面光沢度)は90.3%、インク吸収層側の面をJIS-B-0610に従って測定した時の断面曲線から得られるカットオフ値0.8mmの条件で導かれるる波うねり曲線について基準長2.5mmとしてる波最大うねりを測定したときの任意の測定点100個で最大うねりが6μm以上の点が1個であり10点平均粗さが1.3μm、インク吸収層側の面のベック平滑度は2100秒であった。

イエローインク Y-1 (高沸点有機溶媒比率: 19.7%)

C. I. ダイレクトイエロー86

ジエチレングリコール

グリセリン

純水(イオン交換水)で100mlに仕上げる。

【0134】

マゼンタインク M-1 (高沸点有機溶媒比率: 21.2%)

下記マゼンタ染料-1

ジエチレングリコール

グリセリン

2.1g

15.3ml

4.4ml

1.8g

13.1ml

8.1ml

【0124】上記のようにして得られた40℃の塗布液を、上記のポリエチレン被覆紙の記録面側に塗布し、塗布皮膜温度が15℃以下に成るようにつつま冷却させた(20秒間)。ついで20℃の風を30秒間、25℃の風を30秒間、35℃の風を60秒間、更に45℃の風を120秒間順次吹き付けて乾燥し、さらに25℃、相対湿度50%の雰囲気を通過させて調湿して記録用紙-1を作製した。

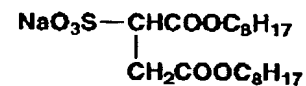
【0125】次に、記録用紙-1において、シリカを1次粒径が13nmのものおよび20nmのものに変更し、記録用紙-1と同様にして記録用紙-2および記録用紙-3を作製した。

【0126】上記の様にして得られた記録用紙を38℃、相対湿度40～60%で5日間保存した。

【0127】

【化1】

界面活性剤-1



【0128】上記記録用紙-1～3の各々について、乾燥膜厚、2次粒子の平均粒径、空隙容量、および光沢度を測定し、表1に示す結果を得た。

【0129】なお、2次粒子の平均粒径は各記録用紙の表面を電子顕微鏡で観察し、各々の記録用紙の任意の100個の粒子について、それぞれその投影面積を求めてその面積に等しい円を仮定した時の直径として個々の粒子の粒径を求め、100個の粒子の粒径の単純平均として各記録用紙の2次粒子の平均粒径を求めた。

【0130】また、空隙容量は、熊谷理機工業株式会社製、Bristow試験機II型(加圧式)を使用し、接触時間2秒間における転移量を空隙容量として求めた。

【0131】光沢度は、日本電色工業株式会社製変角光度計(VGS-101DP)で75度鏡面光沢を測定した。

【0132】一方、インクジェット記録液-1用として以下の組成のインクを調整した。

【0133】〔記録液-1〕

純水（イオン交換水）で100mlに仕上げる。

【0135】

シアンインク C-1（高沸点有機溶媒比率：20.3%）

C. I. ダイレクトブルー199

2.8g

ジエチレングリコール

13.1ml

グリセリン

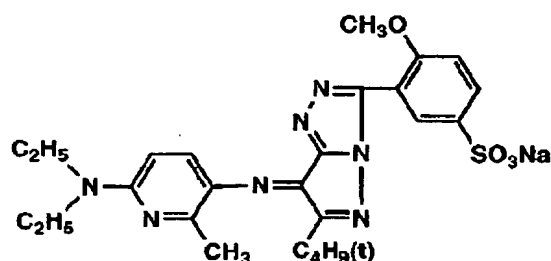
7.2ml

純水（イオン交換水）で100mlに仕上げる。

【0136】

【化2】

マゼンタ染料-1



【0137】上記インク液を使用して、ピエゾ振動子によってインクを吐出させるオンデマンド型インクジェット記録ヘッド（ノズル径＝25μm、各インクとも液滴直径＝約27μm、液滴容積＝約10×10⁻⁶μlになるように吐出条件をそれぞれ調整した。）によって吐出密度を720dpi（吐出間隔＝約35μm）で記録用紙-1～3にインクジェット記録した。この時の最大吐出インク量はインク1色当たり約8.1ml/m²であった。イエロー、マゼンタおよびシアンインクを同時に最大吐出させた時の量は24.3ml/m²である。

【0138】上記の記録用紙-1～3およびインクジェット記録液を用いて、乾燥性と印字後の皮膜強度を以下の方法により評価した。

【0139】（1）乾燥性

上記インクジェットプリンターでイエロー、マゼンタ、およびシアンの各色を同時に最高吐出条件で印字後、23℃、相対湿度65%で30分間保存してから80g/m²の上質紙を200枚重ねて1昼夜保存しインク転写性を以下の基準で調べた。

【0140】

◎：全く転写なし

○：わずかに染料の転写の跡が残るが画像そのものは殆ど変化ない

△：転写痕跡が大きく画像も表面が失透状態になる

×：紙とインク吸収性層の接着が大きく紙が綺麗に剥がせない

また、印字後、同じ条件で24時間保存してから紙を重ねて同様の評価も合わせて行った。

【0141】（2）印字後の皮膜強度

（1）の乾燥性評価と同じ条件で3色同時のベタ印字後2日間放置してから、23℃、相対湿度80%の環境で、引掻強度試験機（ヘイドン・トライボギア、新東科学株式会社製）を用い、先端が0.3mmのサファイヤ針に0～100gの連続荷重をかけ皮膜強度を試験し、皮膜が破壊される強度を皮膜強度として求めた。

【0142】この評価方法で概ね30g以上であれば実用上十分高い皮膜強度を有していると言える。

【0143】上記の結果について、表1に示す。

【0144】

【表1】

記録用紙	2次粒子粒径	乾燥膜厚 (μm)	空隙容量 (ml/m^2)	空隙率 (%)	V/H	光沢度	乾 燥 性		印字後 皮膜強度
							30分後	24時間後	
1 (本発明)	60 μm	40	25.2	63	5.0	69%	◎	◎	90 g
2 (本発明)	140 μm	41	24.7	60	4.9	52%	◎	◎	>100 g
3 (比較例)	230 μm	42	25.4	60	5.1	14%	◎	◎	>100 g

V/H: 最大インク吐出時高沸点有機溶媒量 (5.0ml) に対する空隙容量比率 (%)

【0145】表1に示す結果から、記録用紙-3を用いた場合、2次凝集粒子が200nmを超えて光沢性が大きく低下しているが、記録用紙-1、2はいずれも高い光沢性を有している。特に2次粒子の粒径が100nm

【0146】一方、記録用紙-1～3において、本実施例のインクジェット記録においては、いずれもV/H、すなわち最大インク吐出時の高沸点有機溶媒量に対して4.9～5.1倍の空隙を有しており、良好な乾燥性を有する。

【0147】以上から、記録用紙-1および2を用いた本発明の記録方法に従えば、高い光沢性と良好な乾燥性、印字後の高い皮膜強度を両立できることがわかる。

【0148】実施例2

実施例1で使用したインクジェット記録液-1を以下の記録液-2に変更し、ヘッドから吐出される液滴量を実施例1と同じ量になるように調整し、記録用紙-1～3を用いて実施例1と同様にして乾燥性と印字後の皮膜強度を評価して表2に示す結果を得た。

【0149】〔記録液-2〕

イエローインク Y-2 (高沸点有機溶媒比率: 26.3%)

C. I. ダイレクトイエロー86 2. 1 g
ジエチレングリコール 22. 3 ml
グリセリン 4. 0 ml
純水 (イオン交換水) で100mlに仕上げる。

【0150】

マゼンタインク M-2 (高沸点有機溶媒比率: 29.8%)

マゼンタ染料-1 1. 8 g
ジエチレングリコール 22. 0 ml
グリセリン 7. 8 ml
純水 (イオン交換水) で100mlに仕上げる。

【0151】

シアンインク C-2 (高沸点有機溶媒比率: 29.7%)

C. I. ダイレクトブルー199 2. 8 g
ジエチレングリコール 24. 6 ml
グリセリン 5. 1 ml
純水 (イオン交換水) で100mlに仕上げる。

【0152】

【表2】

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記録用紙	V/H	乾 燥 性		印字後 皮膜強度
		30分後	24時間後	
1 (本発明)	3.6	◎	◎	60 g
2 (本発明)	3.5	◎	◎	70 g
3 (比較例)	3.6	◎	◎	80 g

V/H：最大インク吐出時高沸点有機溶媒量（7.0ml）に対する
空隙容量比率（％）

【0153】表2に示す結果から、インク溶媒量を増加させて、空隙容量が最大インク吐出時の高沸点有機溶媒の3.5～3.6倍程度に低下しても、記録用紙-1、2を用いた本発明の記録方法に従えば、印字直後の皮膜強度が実施例1よりは若干低下するものの、実用上十分満足すべきレベルにある。

【0154】比較例-1

イエローインク Y-3（高沸点有機溶媒比率：36.4％）

C. I. ダイレクトイエロー86

2. 1 g

ジエチレングリコール

31. 8 ml

グリセリン

4. 6 ml

純水（イオン交換水）で100mlに仕上げる。

【0156】

マゼンタインク M-3（高沸点有機溶媒比率：37.8％）

マゼンタ染料-1

1. 8 g

ジエチレングリコール

32. 6 ml

グリセリン

5. 2 ml

純水（イオン交換水）で100mlに仕上げる。

【0157】

シアンインク C-3（高沸点有機溶媒比率：37.2％）

C. I. ダイレクトブルー199

2. 8 g

ジエチレングリコール

31. 3 ml

グリセリン

5. 9 ml

純水（イオン交換水）で100mlに仕上げる。

【0158】

【表3】

記録用紙	V/H	乾 燥 性		印字後 皮膜強度
		30分後	24時間後	
1 (比較例)	2.8	×	△	20 g
2 (比較例)	2.7	×	△	25 g
3 (比較例)	2.8	△	△	30 g

V/H：最大インク吐出時高沸点有機溶媒量（9.0ml）に対する
空隙容量比率（％）

【0159】本比較例は、最大インク吐出時の高沸点有機溶媒に対して3倍以下にした場合であるが、記録用紙-1～3のいずれも乾燥性が実施例1、2より大きく低下し、また、印字後の皮膜強度も特に光沢度の高い記録用紙で悪化し実用上問題を生じかねないレベルにあることがわかる。

【0160】実施例3

実施例1で使用了インクジェット記録液-1を以下の記録液-3に変更し、ヘッドから吐出される液滴量を実施例1と同じ量になるように調整し、記録用紙-1～3を用いて実施例1と同様にして乾燥性と印字後の皮膜強度を評価して表3に示す結果を得た。

【0155】〔記録液-3〕

実施例1で作製した記録用紙-1～3において、それぞれの塗布液を用いて湿润膜厚をそれぞれ約20%増加させて記録用紙-1～3と同様にして記録用紙-1A、2A、3Aを作製した。

【0161】実施例1と同様にして、2次粒子粒径、乾燥膜厚、空隙容量および光沢度を測定した。

50 【0162】一方、実施例1で使用了インクジェット記

録装置を使用し、記録液として比較例1で使用した記録液を用いてインクジェット記録を行い、実施例1と同様に乾燥性と印字後の皮膜強度を調べた。結果を表4に示す。

す。

【0163】

【表4】

記録用紙	2次粒子粒径	乾燥膜厚 (μm)	空隙容量 (ml/m^2)	空隙率 (%)	V/H	光沢度	乾 燥 性		印字後 皮膜強度
							30分後	24時間後	
1 A (本発明)	60 μm	48	30.2	63	3.4	84%	◎	◎	50 g
2 A (本発明)	140 μm	48	30.5	63	3.4	50%	◎	◎	60 g
3 A (比較例)	230 μm	49	30.1	61	3.3	10%	◎	◎	60 g

V/H：最大インク吐出時高沸点有機溶媒量 (9.0ml) に対する空隙容量比率 (%)

【0164】表4から塗布時の湿润膜厚を増大することにより乾燥膜厚と空隙容量は湿润膜厚にほぼ比例して増加するが光沢性が若干低下する傾向がある。

【0165】これは詳細に見ればインク吸収性層の表面にわずかのひび割れ状のクラックが塗布乾燥時に生じているためである。

【0166】表4の結果から高沸点有機溶媒を高濃度で含有するインクを使用した場合であっても、記録用紙の空隙量が最大インク吐出時の高沸点有機溶媒量の3倍を越える場合には良好な乾燥性と印字後の皮膜強度を維持し、しかも2次粒子の平均粒径が200nm以下である記録用紙-1、2を使用した場合には高い光沢性も達成していることがわかる。

【0167】比較例2

実施例1で使用したインクジェット記録装置においてイン

クジェット記録ヘッドをノズル径=30 μm 、各インクの吐出される液滴径が約32 μm 、液滴容積=約 $1.8 \times 10^{-6} \mu\text{l}$ になるように吐出条件をそれぞれ調整したヘッドに変えた(記録液は実施例3で使用了のものを使用した)。また、吐出密度を600dpi(吐出間隔=42 μm)で実施例3で使用了の記録用紙-1A~3Aにインクジェット記録した。この時の最大吐出インク量はインク1色当たり約10.2 ml/m^2 であった。イエロー、マゼンタおよびシアンインクを同時に最大吐出させた時の量は30.6 ml/m^2 である。

【0168】実施例1と同様にして乾燥性と印字後の皮膜強度を評価し、表5に示す結果を得た。

【0169】

【表5】

記録用紙	空隙容量	V/H	乾 燥 性		印字後 皮膜強度
			30分後	24時間後	
1 A (比較例)	30.2	2.7	×	△	15 g
2 A (比較例)	30.5	2.7	×	△	20 g
3 A (比較例)	30.1	2.7	△	○	25 g

V/H：最大インク吐出時高沸点有機溶媒量 (11.3ml) に対する空隙容量比率 (%)

【0170】また、表5の結果から、実施例3で使用了の記録用紙と記録液を使用中にも、液滴径の増大により、吐出間隔をこれに対応させても記録用紙としての全体の吐出量が増大したために最大インク吐出時の高沸点有機溶媒量に対して空隙量が3倍以下になったために、乾燥性と印字後の皮膜強度が低下した。

【0171】実施例4

実施例1で作製した記録用紙-1~3において、それぞれの湿润膜厚を約40%増加させた記録用紙-1B~3

Bを記録用紙-1~3と同様にして作製した。

【0172】記録用紙-1B、2B、3Bの2次粒子の粒径、空隙容量、および光沢度の結果を表6に示す。

【0173】更に比較例2で用いたインクジェット記録装置で、比較例1で用いた記録液を用いて比較例2と同様に評価し、表6に示す結果を得た。

【0174】

【表6】

記録用紙	2次粒子粒径	乾燥膜厚 (μm)	空隙容量 (ml/m^2)	空隙率 (%)	V/H	光沢度	乾 燥 性		印字後 皮膜強度
							30分後	24時間後	
1 B (本発明)	60 μm	55	35.4	64	3.1	56%	○	◎	40g
2 B (本発明)	140 μm	56	35.8	64	3.2	42%	○	◎	50g
3 B (比較例)	240 μm	56	35.6	64	3.2	9%	○	◎	60g

V/H: 最大インク吐出時高沸点有機溶媒量 (11.3ml) に対する空隙容量比率 (%)

【0175】表6の結果から、塗布膜厚のさらなる増大により空隙量が増大してくるが光沢性は更に低下する。但し、記録用紙-1B、および2B程度ならば実用上は何とか許容し得るレベルにあるが3Bの光沢は完全に消滅しいわゆるマット面になっている。

【0176】また、表6の結果から、乾燥性や印字後の皮膜強度は実施例1、2に比べれば低下しているものの、比較例1、2に比べれば良好な結果を示している。

【0177】実施例5

実施例1で作製した記録用紙-1~3において、硬膜剤としてほう砂を添加しない記録用紙-1C、2C、3Cを作製した。

【0178】実施例1で作製した記録用紙において、水溶液(II)のポリビニルアルコール濃度を4%に変更した以外は記録用紙-1~3と同様にして記録用紙-1D、2D、3Dを作製した。

【0179】実施例1で作製した記録用紙-1~3にお

いて、ポリビニルアルコールを平均重合度が約1700でケン化度が88%のポリビニルアルコールに変更した以外は記録用紙-1~3と同様にして記録用紙-1E、2E、3Eを作製した。

【0180】また、実施例1で作製した記録用紙-1~3において、ポリエチレン被覆紙上に塗布後、乾燥時に冷却することなく70~100℃の風を吹き付けて乾燥して記録用紙-1F、2F、3Fを作製した。

【0181】上記の各記録用紙を実施例1と同様にして、乾燥膜厚、空隙容量、および光沢度を調べた。結果を表7に示す。

【0182】一方、実施例2で使用した記録液を用い、実施例2と同様にして乾燥性および印字後の皮膜強度を調べた。結果を表7に示す。

【0183】

【表7】

記録用紙	2次粒子粒径	乾燥膜厚 (μm)	空隙容量 (ml/m^2)	空隙率 (%)	V/H	光沢度	乾 燥 性		印字後 皮膜強度
							30分後	24時間後	
1 C (本発明)	60 μm	41	24.4	59	3.5	61%	◎	◎	50g
2 C (本発明)	140 μm	42	24.0	57	3.4	49%	◎	◎	50g
3 C (比較例)	230 μm	41	24.7	60	3.5	11%	◎	◎	60g
1 D (比較例)	50 μm	37	17.9	48	2.6	73%	×	△	10g
2 D (比較例)	130 μm	38	18.3	48	2.6	59%	×	△	10g
3 D (比較例)	220 μm	37	18.4	50	2.6	36%	×	△	20g
1 E (本発明)	60 μm	40	24.6	62	3.5	55%	◎	◎	60g
2 E (本発明)	140 μm	41	25.7	63	3.7	43%	◎	◎	80g
3 E (比較例)	230 μm	41	25.9	63	3.7	8%	◎	◎	>100g
1 F (比較例)	60 μm	35	17.8	51	2.5	51%	×	△	10g
2 F (比較例)	140 μm	36	18.3	51	2.6	40%	×	△	10g
3 F (比較例)	230 μm	36	19.5	54	2.8	10%	×	○	30g

V/H: 最大インク吐出時高沸点有機溶媒量 (T.0ml) に対する空隙容量比率 (%)

【0184】表7の結果から、硬膜剤としてほう砂を取り除いた場合(記録用紙-1C~3C)、記録用紙-1~3に比較して、印字後の皮膜強度や光沢性が若干低下しているが、空隙容量や乾燥性は殆ど変わらない。

【0185】記録用紙-1においてポリビニルアルコールの使用量を2倍にして、無機微粒子に対する親水性バ

インダーの比率を1/2に下げた場合、光沢性は改善されているが、空隙容量が約2/3となり高沸点有機溶媒量に対する空隙容量が3倍以下になり、乾燥性や印字後の皮膜強度が大きく低下している。

【0186】記録用紙-1において、ポリビニルアルコールを平均重合度のより低いものに変えた場合には光沢

度が稍低下しているが概ねほう砂を取り除いた時に近い乾燥性と皮膜強度を有している。

【0187】記録用紙-1の製造の際に塗布後冷却してセットさせることなく加熱乾燥した試料では、空隙容量が低下して乾燥性や皮膜強度が悪化しただけでなく、ひび割れに伴う光沢性の低下が認められた。

【0188】

【発明の効果】以上、本発明のインクジェット記録方法を用いれば、高い最高濃度と鮮明度を有し、高光沢性の高画質のカラー画像が得られる。また、印字直後に表面の皮膜の強度が十分強く取り扱い性が優れたフルカラー画像が得られる。